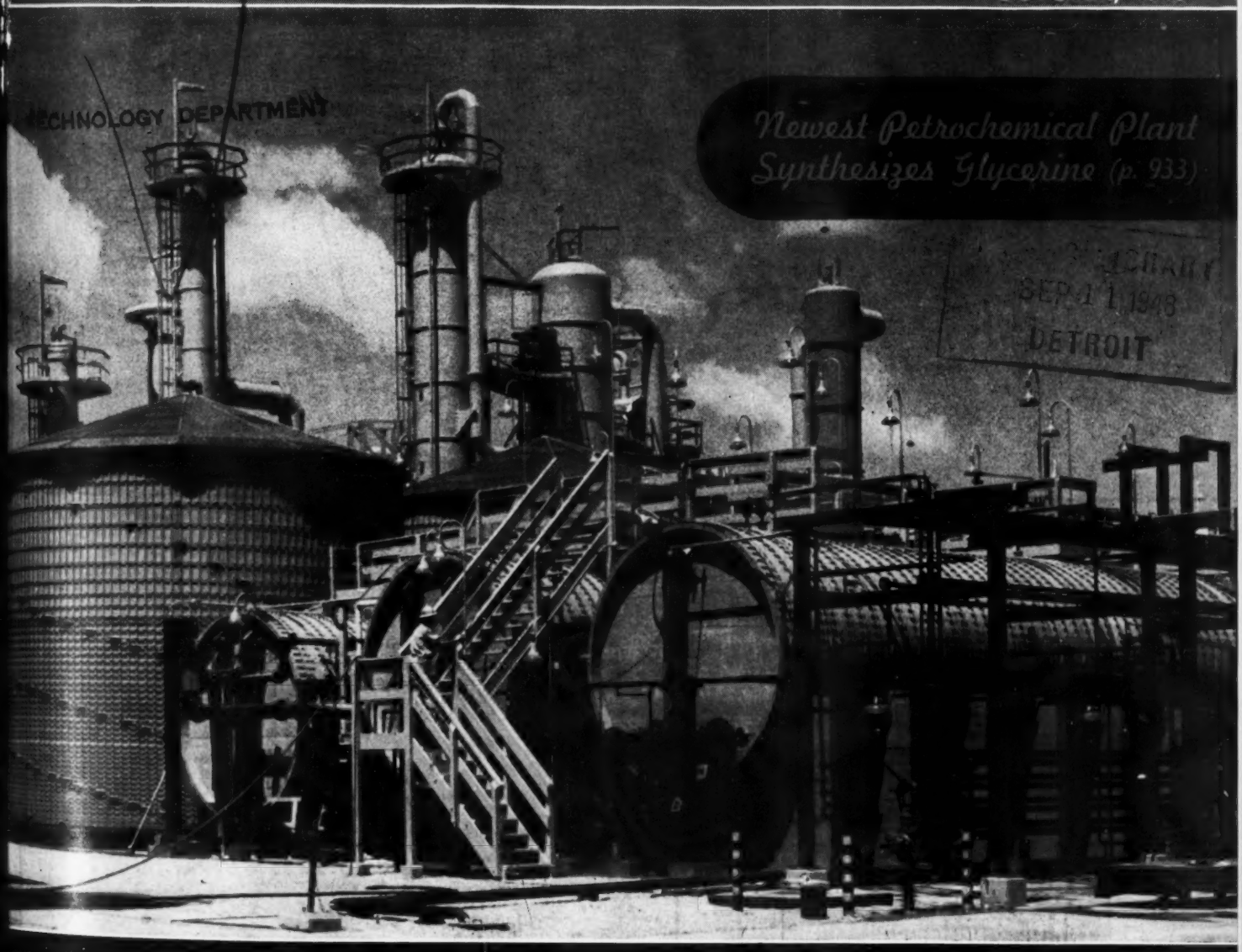
PETROLEUM PROCESSING

VOLUME 3, NUMBER 10 OCTOBER, 1948

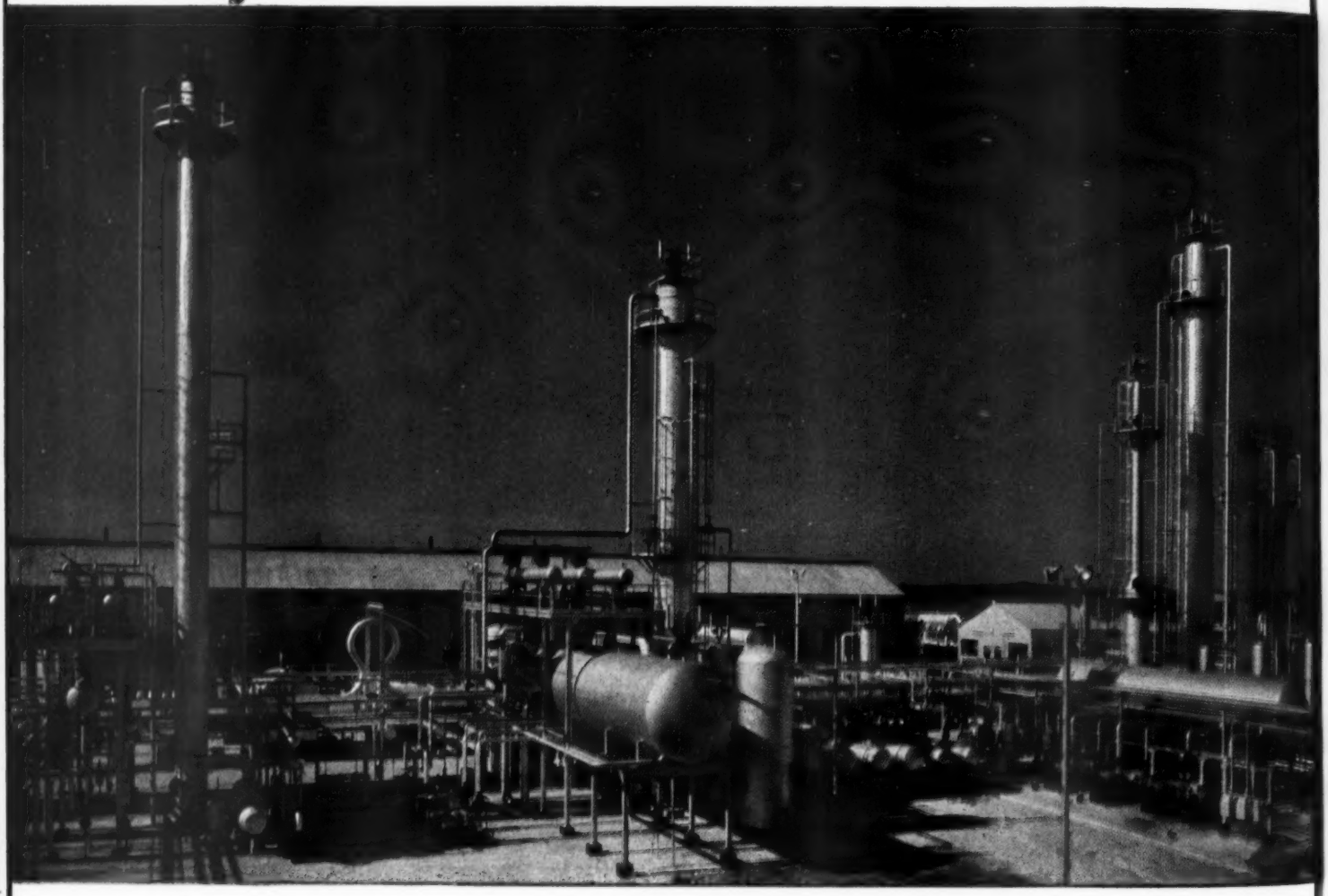


Newest Petrochemical Plant Synthesizes Glycerine (p. 933)

FORMERLY MONTHLY TECHNICAL SECTION OF NATIONAL PETROLEUM NEWS

The WEST RANCH GAS PROCESSING PLANT

Built by HUDSON



On the huge cattle ranch of the West family near Vanderbilt, Texas, Magnolia Petroleum and other operators have developed a major oil and gas field. The West Ranch plant, designed and constructed by Hudson Engineering Corporation, in collaboration with Magnolia Petroleum Company, is an instrument to carry out the program of the Texas Railroad Commission and all forward looking oil operators to minimize the waste of gas.

About eighty million cubic feet of gas daily is processed in this plant to recover about 50,000 gallons per day of liquid hydrocarbons. The gas remaining after extraction of the liquids is used as industrial fuel.

Hudson Engineering Corporation, qualified by many years of experience in completing projects such as the West Ranch plant, offers its services for major gas processing projects in any part of the world.

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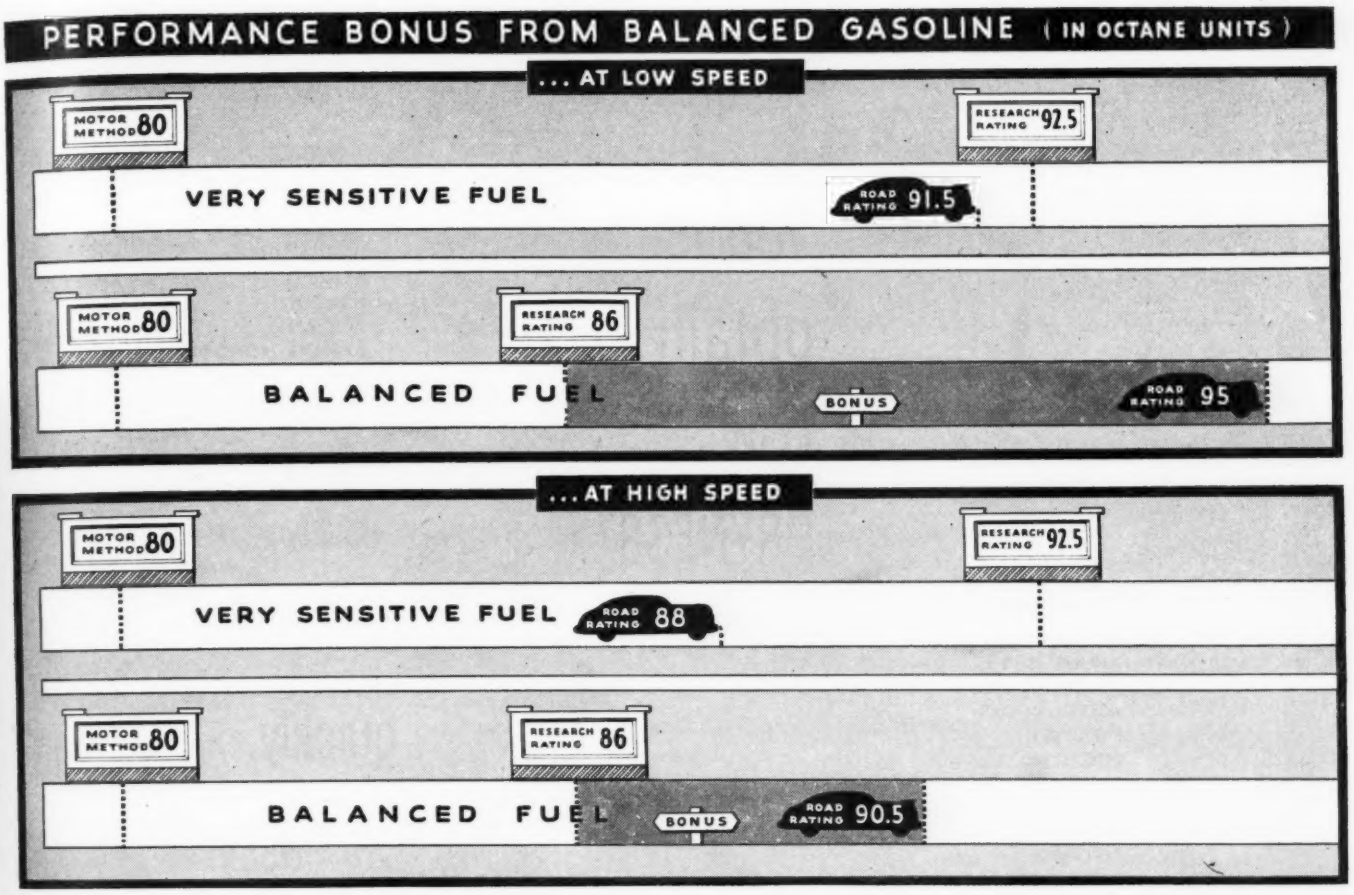
GAS COMPRESSOR STATIONS • CYCLING PLANTS • GAS DEHYDRATION PLANTS • NATURAL GASOLINE PLANTS FRACTIONATION UNITS • CRUDE TOPPING UNITS • PRESSURE MAINTENANCE PLANTS • HYDROGEN SULPHIDE REMOVAL PLANTS • ATMOSPHERIC AND VACUUM DISTILLATION UNITS



*Boosting road performance with balanced gasoline**

WHAT are the possibilities of balanced gasolines—and what do they mean to long-range refinery planning?

To help refiners find the answer, Ethyl Corporation utilizes its unique position between the automotive and petroleum industries.

Over the past ten years, Ethyl's work on fuels and engines has demonstrated that the hydrocarbon distribution throughout the boiling range of a gasoline is fundamental to its performance on the road. This hydrocarbon distribution may be revealed in part by the "jump," or sensitivity—Research method octane rating minus Motor method rating—but it is becoming increasingly clear that these conventional laboratory ratings may not indicate the quality of fuels in actual service.

The chart illustrates the performance possibilities to be realized through balancing a gasoline. These two non-leaded fuels—a very sensitive gasoline and a balanced gasoline—have equal Motor method ratings of about 80. The very sensitive gasoline has a Research rating of 92.5, giving it a sensitivity of 12.5. The balanced gasoline rates only 86 by the Research method, giving it a sensitivity of just 6 octane numbers—less than half that of the very sensitive fuel.

Yet when these fuels are rated on the road, the balanced blend is far ahead. It rates some 9 octane numbers above its Research value at low speeds, and continues to rate above its Research octane number even at high speeds. The very sensitive gasoline, on the other hand, rates just slightly under its Research value at low speeds and substantially under at high speeds.

These characteristics are particularly important inasmuch as development programs indicate that vehicles of the future will have high speed octane requirements considerably above those of present-day automobiles. Highly sensitive fuels often tend to drop off rapidly in antiknock quality on the road as engine speed increases.

It is not Ethyl's objective to advise oil companies on refinery operation. This particular research program is intended only to indicate the unusual possibilities of balanced gasoline, and to suggest broadly how refiners may achieve similar results.

**A balanced gasoline has a distribution of hydrocarbon types with respect to boiling range so controlled that it will give optimum road antiknock quality and optimum road tetraethyllead susceptibility at all engine speeds.*

Serving The Progressive Petroleum Industry Through Research

ETHYL CORPORATION
RESEARCH LABORATORIES

1600 West Eight Mile Road, Detroit, Michigan 2600 Cajon Road, San Bernardino, California

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MELTED WAXES
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BUTYL ACETATE
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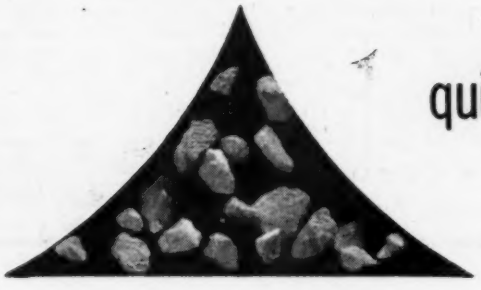

ALCOA Activated Aluminas are among the most effective and efficient desiccants available for the dehydration of liquids and gases. Dew points as low as *minus* 100° F.—and even lower—may be obtained, and under normal circumstances, ALCOA Activated Aluminas can be used for an almost indefinite number of drying cycles.

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Besides their use for dehydration, ALCOA Activated Aluminas adsorb certain gases and vapors from gaseous mixtures and serve as catalysts and catalyst carriers. They are used in the liquefaction of gases, and for the maintenance of transformer and lubricating oils.

We should like to tell you more about these efficient, solid-type desiccants. Write to: ALUMINUM COMPANY OF AMERICA, CHEMICALS DIVISION, 1780 Gulf Bldg., Pittsburgh 19, Pa.

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VOLUME 3
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OCTOBER, 1948
PUBLISHED
MONTHLY

PETROLEUM PROCESSING

OTHER PLATT PUBLICATIONS:
NATIONAL PETROLEUM NEWS
OILGRAM NEWS
OILGRAM PRICES
PLATTS'S OIL PRICE HANDBOOK

Covering the Management, Design, Operation, Equipment, Products of Plants Processing Crude Oil and Natural Gas into Fuels, Lubricants, Chemicals

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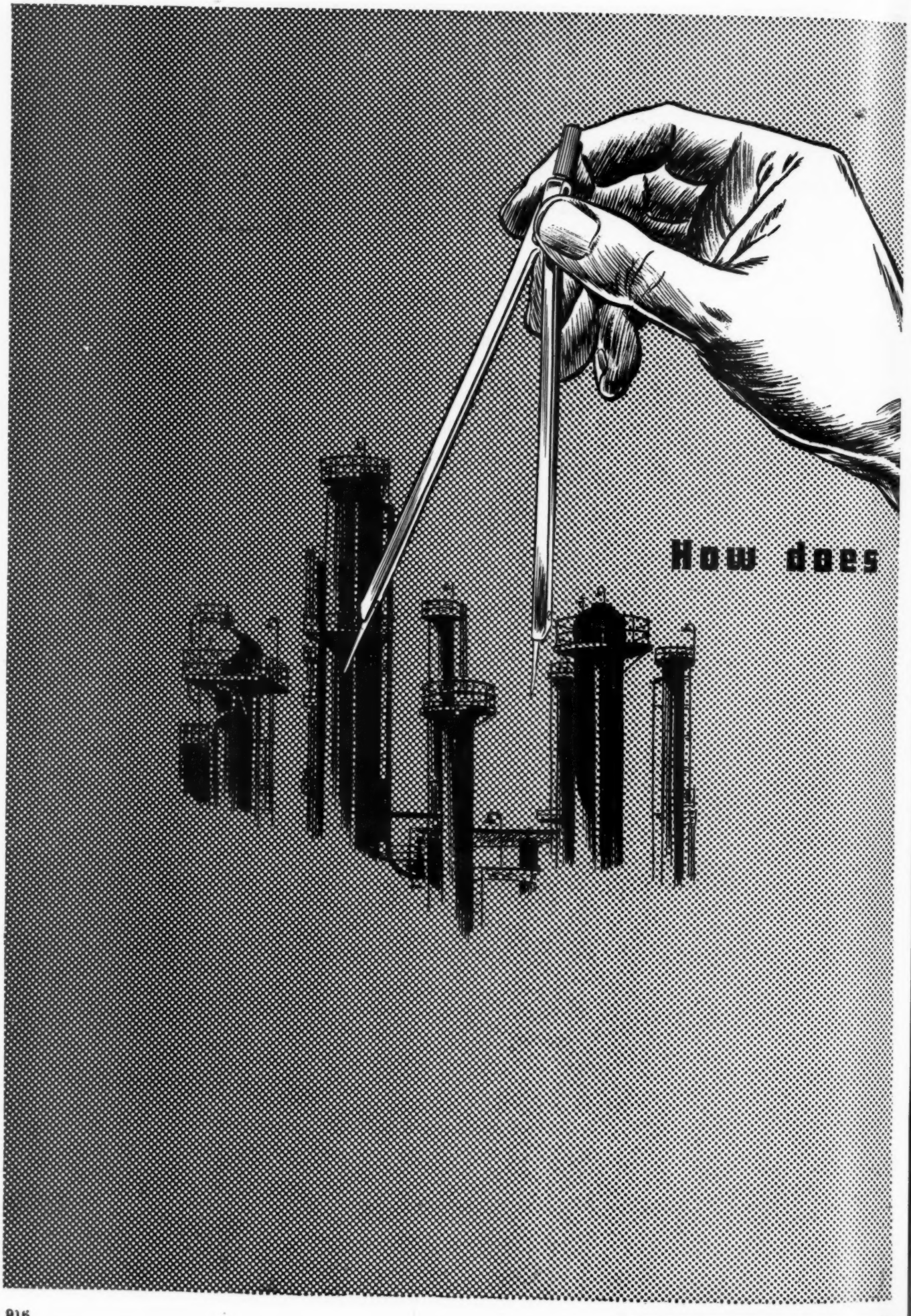
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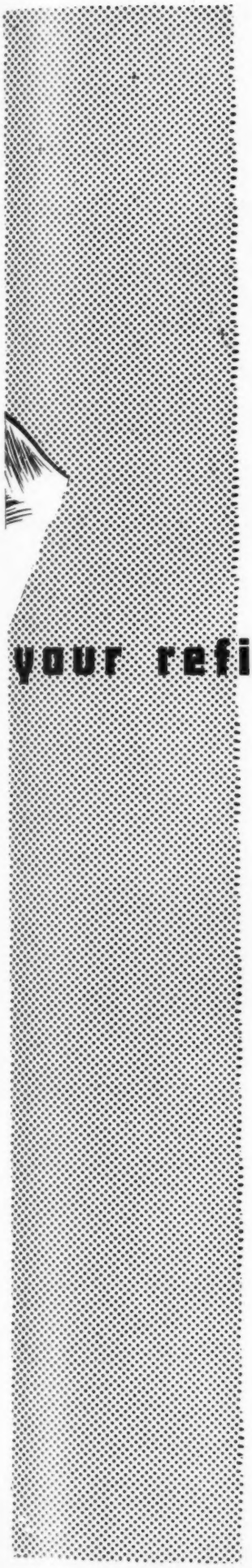

your refinery measure competitively?

With demand still far ahead of supply . . . with your refinery and those of your competitors operating at peak capacity . . . with no doubt as to your ability to market all of your production . . . actual experience certainly will not give you the answer. But what about tomorrow, when new facilities are placed in operation?

To meet the coming competitive market, you must have the answer today.

Universal can give you that answer *now* . . . plus assistance in maintaining the efficiency and economy of your operation in the face of future competitive problems.

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UOP

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LABORATORIES: RIVERSIDE, ILLINOIS

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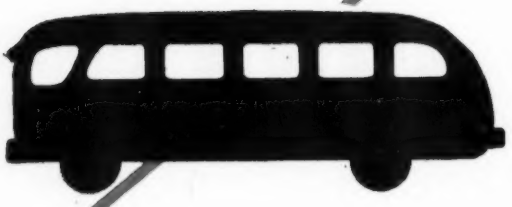

DETERGENCY—maximum engine cleanliness

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Consult our technical staff for complete information or assistance in the use of AEROLUBE Additives to improve your Regular, Premium, and Heavy-Duty motor oils.

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What's Happening!

OCTOBER 1
1948

Important Current News Summarized for Refiners

EXPANSION

West Texas will get new natural gasoline plant of 60,000 gals. daily capacity from 10 million cu. ft. of natural gas. Immediate construction in Todd Field is scheduled with Continental Oil Co. as the operator. Refinery Maintenance Co. of Compton, Calif. is the contractor, and completion is anticipated within a year.

Shell Oil Co. has acquired 280 acres of a possible refinery site at Woodbridge, N. J., a township-owned tract on the Rahway River. Tract is part of an area selected by the company as potential location for $100 million refinery planned for East Coast. Shell has not confirmed officially that refinery will be built there, saying only that the site is one of those being considered.

Ashland Oil & Refining Co.'s modernization of its Thermofor catalytic cracking unit is nearing completion. Contract, held by Catalytic Construction Co., calls for conversion to solid bed design, a new catalyst distributing system, and increasing kiln carbon burning capacity by addition of two zones to the existing eight.

Globe Oil & Refining Co. has entered into an agreement with Universal Oil Products Co. for the installation of a Fluid catalytic cracking unit at its Lemont, Ill., refinery. Using existing feed preparation equipment, the unit will handle 6,000 b/d of heavy vacuum gas oil at a 50% conversion level.

• • •

REFINERY OPERATIONS

Crude run to stills during September, not including California, dropped off still further from August low points. In week ending Sept. 11, total had reached 5,361,000 b/d.

Crude production in September also tapered off after hitting new highs in August. Low point was reached week ending Sept. 18 at 5,294,350 b/d, including California production which was materially affected by strike conditions.

Progress was made in California as Shell Oil resumed operation of Wilmington refinery on Sept. 20, and Richfield and The Texas Co. said Sept. 28 that operations were about to be resumed shortly, leaving Tide Water Associated still unaccounted for. Elsewhere on the labor front, negotiations between OWIU and Ohio Standard had been recessed indefinitely pending further call by federal mediator.

• • •

MARKETS, PRICES

Sharp price reductions for many refined products were noted during the past month due to further easing of supplies. Relaxation of gasoline allocations, which started in August, carried over into September. Supplies of distillate fuels were in sufficient volume that the usual fall open market demand was lacking. Movement was almost entirely from regular supplier to regular customer. Heavy fuel storage tanks were spilling over. Lack of foreign demand depressed prices for lubes and wax.

Price highlights of the month: Western Pennsylvania bright stocks and neutrals down in amounts ranging from 6 to 10c per gal.; Midcontinent neutrals off 2c; crude scale wax prices down 1.5c per lb.; Oklahoma No. 6 fuel offered at $1.80 per bbl., off 40c.

• • •

TRANSITION

Petrol Refining, Inc., a new $10 million corporation, has been formed by an independent refinery, Petrol Terminals, Inc. and three East Coast farmer cooperatives—Southern States Co-operative, Pennsylvania Farm Bureau Co-op Assoc., and Co-operative Grange League Federation Exchange. New company has three tankers, assured crude supply of million bbls./month, and refineries at Texas City and Beaumont with combined capacity of 30,000 b/d.

Danciger Oil & Refining Co.'s 7,500 b/d Longview, Texas, refinery was purchased Sept. 4 for "about $1 million" by W. C. Berry, oil operator, and his associates, Robert Baker and John Gibson, all of Tulsa. Deal included Longview gathering line, 88-acre site and storage facilities. Cordova gathering line was not included in purchase, but will be leased. Plant, idle three years, was "bought as a speculation" and new owners have no immediate plans for its use.

Northwestern Refining Co., St. Paul Park, Minn., has purchased a refinery at St. Elmo, Ill., about 70 miles east of St. Louis, formerly operated by Allied Oil Corp. of Chicago. Equipment includes a 5,000 b/d skimming unit and 2,000 b/d Thermal cracking

Information on these pages is obtained through the nation-wide news coverage services of PLATT'S OILGRAM NEWS

unit. Officials expect plant to be operating about mid-November. Purchase represents first time nine year-old company has expanded refining and marketing activities into Illinois.

• • •

PRODUCTS

A revised Commercial Standard for Fuel Oils, identified as CS12-48, has been adopted by the National Bureau of Standards, with date effective for new production as of September 25, 1948. The specifications cover five grades of fuel oil, Nos. 1, 2, 4, 5, and 6. Technical requirements are identical in substance with Tentative Specifications for Fuel Oils, ASTM Designation: D 396-48T.

Full dieselization of all U. S. railroads would result in less fuel oil being used by locomotives than is consumed today, according to Robert B. McColl, president, American Locomotive Co. He pointed out that approximately 7,000 of the existing 35,000 steam locomotives are oil burners. On the average an oil-burning steam locomotive uses many times more oil than a diesel-electric. Current daily consumption by U. S. railroads is 227,485 bbls. fuel oil; with complete dieselization, only 170,343 bbls. of diesel oil would be estimated requirement. McColl predicted 20,000 diesel-electric locomotives will be built in next ten years.

• • •

PROCESSES

Houdriflow, an improved catalytic cracking process developed jointly by Sun Oil Co. and Houdry Process Corp., will be a feature of $16-million expansion program at Sun's Toledo, Ohio, refinery. Construction, by Catalytic Construction Co., Philadelphia, a Houdry Process subsidiary, will also include a large gas recovery and gasoline stabilization plant, new polymerization plant, crude distillation unit, and vacuum flash unit. Program will almost double capacity of present 35,000 b/d plant. Completion is expected by end of 1949.

Key unit in new continuous lime soap grease process is a rapid soap cooker which in 45 minutes completes the 3½-hour job of the old pressure kettle. Large scale production will begin early this fall at Esso Standard Oil Co.'s Baltimore refinery.

• • •

RESEARCH

Seven oil companies are in group which has signed agreements with Bureau of Mines under which they will be supplied limited quantities of oil shale and shale oil for experimental work in exchange for information on results. They are Sinclair, Standard Oil Development, Union, Socony-Vacuum, Shell Development, Phillips, and Gulf Research & Development. Complete group also includes General Aniline & Film Corp., Godfrey L. Cabot, Inc., and Montana State College. Bureau said other companies or institutions can make applications for shale oil or oil shale, and should write to Boyd Guthrie, chief, Oil-Shale Demonstration Plant, Bureau of Mines, Rifle, Colo., telling quantity desired, purpose for which it is to be used, and proposed shipping arrangement.

Humble Oil & Refining Co. states construction has begun on a new research laboratory building at Baytown refinery, centralizing activities now scattered over three different locations. Building, which will house 115 research personnel, will be erected by Knutson Construction Co., Houston; completion is scheduled for late 1949.

Stanolind Oil & Gas Co. has shelved for at least a year its plans to begin construction of a new research laboratory at Tulsa, because of high and unstable costs and difficulty in obtaining essential materials, according to Executive Vice-President A. L. Solliday. Simultaneously, company revealed purchase of 20 more acres for new laboratory site, just west of 60-acre plot already acquire southeast of Tulsa.

• • •

MISCELLANY

Five-year-old suit against Universal Oil Products Co. has been settled out of court. Filed by Dean Caulfield Daily for an original $18.5-million involving patent rights on cracking processes, suit was agreed to for "considerably less" than a million dollars, a party to the suit stated, and said agreement was reached about middle of August. In December, 1947, Federal Judge M. L. Igoe of Chicago, in a memorandum opinion, had indicated final judgment of $650,000 against UOP.

Blame for Los Angeles "smog" conditions was placed on oil refineries, chemical plants, and industries burning fuel oil by L. C. McCabe, director of county air pollution control district. Report stated atmospheric conditions improved after closing of several refineries by strikes, and noted smog continued around General Petroleum's unstruck refinery.

Information on steel industry's distribution pattern is being sought by Senate Small Business (Wherry) Committee by means of questionnaires mailed to 15 largest steel producers. Committee said particular interest is in charting flow of steel pipe and tubing from mills to consumers.

Harry C. Wiess, 61, board chairman of Humble Oil & Refining Co., and one of its founders, died August 26, in his Houston home. A native of Beaumont, Wiess had been associated with the oil industry 39 years, since his graduation from Princeton in 1909.

Important News For Every Oil Man in the United States!

OCTOBER 14 proclaimed OIL PROGRESS DAY!

A day set aside on which your community's attention will be focused on YOU and YOUR BUSINESS!

Here's what this special occasion will mean to you...and what YOU can do to make the most of it!

On October 14, the people in your locality will turn their attention to *you!* For that's the date of Oil Progress Day—the day for you to report the progress you and your industry have made. People will look to YOU on that day—because you are the part of the oil industry best known to the people in your community.

This is your big opportunity to tell how your company is helping to meet the greatest demand in history. Your chance to tell the role your company plays in handling the tremendous amount of oil products being supplied America today. Yes, Oil Progress Day is a wonderful time to tell your neighbors how you serve the community.

You're The One Who Gains!

YOU gain when the public understands the competition in oil—the way you compete with rival firms to win customer approval. For once the public knows the great job you've been doing, they'll understand why your business freedom means MORE OIL FOR THEM! That's why this open house for the oil industry can be of so much benefit to *you!*

Get Ready For Your Big Day!

Right now free material to promote Oil Progress Day is being rushed to your local committee office. Tie in ads ... sample speeches ... booklets ... motion pictures ... employee meeting material ... poster designs ... radio material ... *everything* you need to make Oil Progress Day YOUR DAY!

Get in touch with your local committee office NOW! The address is listed below. Write TODAY so you'll be all set for Oil Progress Day!

OIL INDUSTRY INFORMATION COMMITTEE

District Offices:

ATLANTA	CINCINNATI	KANSAS CITY	NEW YORK
BOSTON	DALLAS	LOS ANGELES	PHILADELPHIA
CHICAGO	DENVER	MINNEAPOLIS	TULSA

Here's how you can benefit from Oil Progress Day in your community

Hold "open house" on October 14 and let people get acquainted with your business. That way, your neighbors will get a new understanding of the problems you face...an understanding that's *bound* to result in more friends for YOU! Tell them how great the need for oil is ... how *hard* you've worked to keep them supplied and still maintain your high standards of quality and service—and you create good will that pays off for *you* and *your firm* in the long run!

Get in touch with your district committee NOW!

They'll make it easy for you to make the most of Oil Progress Day. They'll give you material you can use to tie your business in with this big nation-wide report!

Don't miss this chance to stand out in your community! *Make Oil Progress Day Your Day!*

VESSEL DIVISION

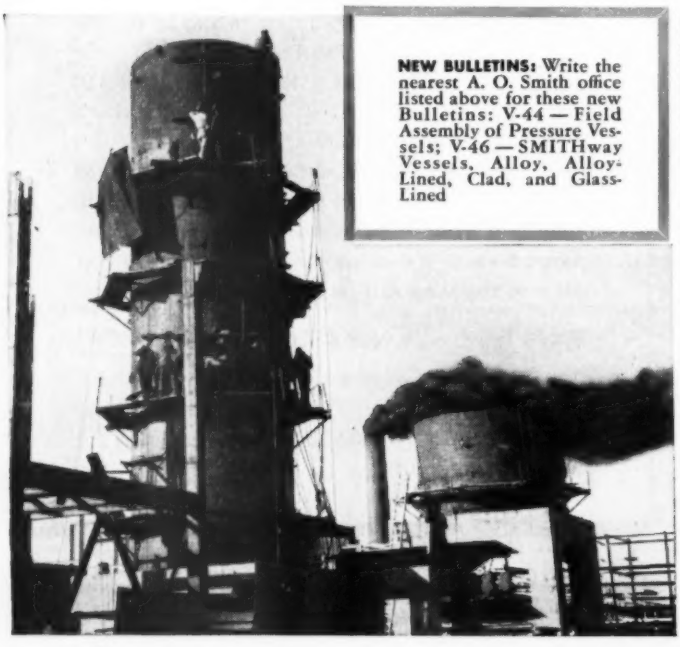
NEWS

A. O. SMITH Corporation

New York 17 • Philadelphia 5 • Pittsburgh 19 • Atlanta 3 • Chicago 4
Tulsa 3 • Houston 2 • Seattle 1 • Los Angeles 14
International Division: Milwaukee 1

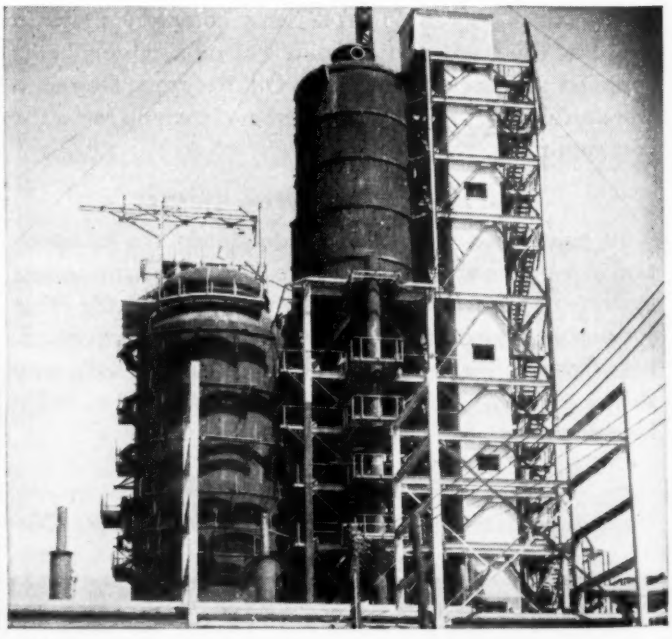
TEAMWORK GETS RESULTS. This is the team that field-erected the SMITHway Vessels for the refinery shown below.

Harold Pollei (right), supervisor of A. O. Smith Field Service, is backed up by the vast metallurgical, welding, spectographic, and electrical laboratory facilities of A. O. Smith in solving the daily technical problems with Harry Drummond (left), job superintendent on the field work, and two of his foremen.



NEW BULLETINS: Write the nearest A. O. Smith office listed above for these new Bulletins: V-44 — Field Assembly of Pressure Vessels; V-46 — SMITHway Vessels, Alloy, Alloy-Lined, Clad, and Glass-Lined

CRUDE OIL UNIT. Left, fractionating column, 14 ft. dia. x 89 ft. 8 in. high, weight 165,000 lb., SMITH-lined with monel and type 405 stainless steel. Right, vacuum column, 22 ft. dia. x 51 ft. high, weighing 183,000 lb., SMITHlined with type 405 stainless steel.



FLUID CATALYTIC CRACKING UNIT NEARING COMPLETION. At left is the regenerator, 20 ft. dia. x 79 ft. 8 in. high, weighing 334,000 lb. Right, the reactor, 22 ft. 6 in. dia. x 62 ft. high, weight 266,000 lb., is carbon moly SMITHlined with type 405 stainless steel.

PETRECO *Electric* DESALTING

DOES MORE than just remove salt...

One of the most important and profitable benefits refiners gain from Petreco Electric Desalting is *increased refining capacity.* This ability to charge more crude results directly from the high efficiency of Petreco Desalting, which

1. Eliminates salt plugging in condensers and tower trays.
2. Reduces corrosion from evolved HCl.
3. Prevents the formation of hard, flinty coke in furnaces.
4. Removes suspended solids such as sand, silt, rust, etc., from the crude charge.
5. Traps and removes slugs of water or B.S. picked up from crude storage.

By forestalling the basic difficulties inherent in plugging, corrosion, coking, foreign solids and B.S. and W. in the crude charge, Petreco Desalting

1. Increases heat exchange efficiency.
2. Reduces mechanical shut-downs caused by erosion and corrosion.
3. Permits high furnace temperatures, deeper cracking.
4. Keeps the refinery on stream longer, reduces down-time.
5. Cuts maintenance and repair costs.

Besides insuring efficient salt removal, PETRECO provides complete service, available replacement parts, engineering cooperation, and laboratory assistance, and the KNOW HOW gained from many years of desalting experience.

For further information, or a conference on your salt problem, just write or call any Petreco headquarters. A Petreco engineer will call on you, at your convenience. Get *all* the facts,—it pays.

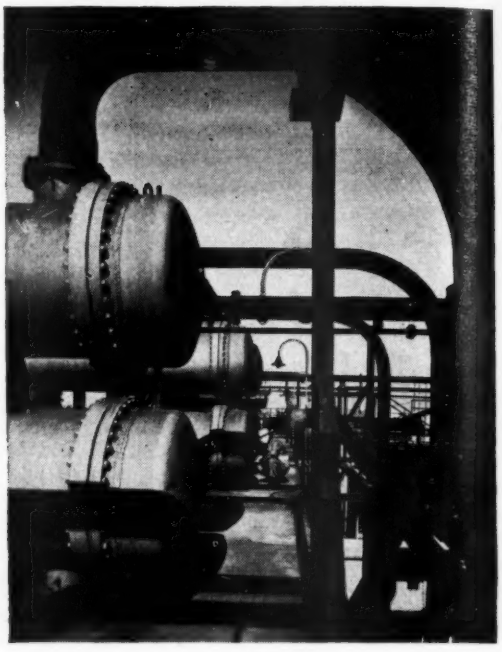
PETROLEUM RECTIFYING COMPANY
5121 S. Wayside Drive, Houston 1, Texas
648 Edison Building, Toledo 4, Ohio
530 W. Sixth Street, Los Angeles 14, Calif.

PETRECO

SPECIALIZED *Electric* PETROLEUM PROCESSES { **DESALTING** / **DEHYDRATING**

PR 48-3

NUMBER 3 IN A SERIES



The "Master" Contract and mechanical engineering time

THE "master" type of contract for refinery modernization and expansion—under which one engineering company takes complete responsibility for all work—nowhere manifests its superiority to greater advantage than in the time-consuming details of mechanical engineering.

First, through confining all engineering within *one* organization it eliminates costly hours spent in coordinating details between several engineering contractors. Further the "master" contract operation eliminates any possibility of expensive job-site alterations when a few of the multitudinous details involved fail to be accurately coordinated among several engineering organizations all working independently.

To get down to a few specifics in the matter of savings through coordination, the "master" contract operation saves time *at the very inception of mechanical engineering*—in the initial problems concerned with the relative locations of the process units, their space and tankage requirements and such provision for future expansion as may be deemed necessary without undue initial investment. The required off-site facilities are usually an important factor in these problems and therefore simultaneous studies must be made of the electric power, steam, fuel gas, water and air distribution systems, all yard oil piping and the various sewers and blowdown systems, before an intelligent decision can be made.

Detailed design of the process units cannot be started until this overall picture has been completed, steam, water and fuel gas pressures and temperatures at the battery limits have been determined, where all incoming and outgoing services and oil and sewer lines should enter and leave each battery limit and their elevations.

All these as well as a veritable host of other important engineering details *must be* integrated between units—not on the basis of greatest ease or economy in the building of any one unit—but on the basis of *overall economy and efficiency of the entire processing plant.*

To obtain such integration to the maximum degree of final efficiency among the various design departments of several engineer-contractors is obviously expecting the impossible from human nature. For it must be borne in mind that each engineer-contractor has developed his organization along lines that suit his particular method of operation. Each has his own particular methods and standards of design, each his own table of specifications. If the impossible is accomplished, it is *still* costly—for since each contractor must wait for information from the other there is time consumed in its accomplishment that could serve either to advance the date of operation of the unit, or lower its cost, or both.

There is still another major overall advantage of the "master" contract operation—beyond the actual dollars-and-cents savings in engineering time. This is in the *uniformity of engineering specifications*—when all work at the job site is handled by *one concern.* Such uniformity results in reduced construction costs since all buildings and structures will be of uniform basic design. Furthermore, such uniformity results in reduced maintenance costs and a smaller spare parts inventory, neither being an inconsequential consideration in these days when maintenance costs are a major factor in establishing processing profits.

by
O. G. PRATT
In Charge of Mechanical Engineering
The M. W. Kellogg Company

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TOMORROW

. . . IN PETROLEUM TECHNOLOGY

Current technological and economic developments discussed here in the light of their future bearing on petroleum refining operations include:

- **Catalytic hydrocarbon-steam reaction under development for fuel gas production.**
- **Petrochemical economics clouded by high petroleum prices.**
- **Stanolind's cancellation of Synthine plant is highly significant.**
- **Oxo process receiving commercial attention.**

Catalytic Hydrocarbon-Steam Reaction Under Development

AS MENTIONED BRIEFLY in the July installment of this series[1], several gas companies and gas industry groups are hard at work on the development of processes that can be used for the production of "peak load gas"—that is, gas that can be economically produced in stand-by equipment, yet which can be mixed with the normal gas sendout without changing the quality or properties of the latter.

Propane-air mixtures in concentrations up to about 22-25% (of the finished gas) have been used in the past to augment regular production, but the high specific gravity of the gas prohibits the use of higher concentrations unless propane-air mixtures of increased thermal content are employed (up to 60% can be tolerated in this manner). However, since customers are billed on a volumetric basis, the use of this gas has obvious economic disadvantages, and the gas industry has therefore been seeking to develop a "carrier gas" for propane or butane which, when mixed with the latter, will have the desired properties yet be economically produced.

One of the promising processes now under study involves the "catalytic reforming" of hydrocarbons—propane, butane, refinery gas, natural gasoline, kerosine, naphthas, gas oils, etc.—to produce a "carrier gas" which can be mixed with propane or butane in sufficient quantities to produce a finished gas of normal sendout characteristics. In this particular process, the terms "catalytic reforming" or "catalytic cracking" are employed in connection with the specific catalytic reaction of steam and hydrocarbons to produce a gas whose principal combustibles are hydrogen and carbon monoxide—similar to water gas. As will be noted, this is essentially the "methane-steam" process long employed for the synthesis of hydrogen for various petroleum and chemical industry processes, the principal evolution being the extension to the use of heavier hydrocarbons and the development of better catalysts.

For example, propane may be converted by means of the catalytic steam-hydrocarbon reaction to yield a carrier gas of low heating value (220-237 Btu/cu. ft., in one experiment), to which sufficient propane can then be added to produce a finished gas of 540 Btu/cu. ft., the normal sendout value. Since the specific gravity of this mixture (0.70) also matches the normal sendout value, the process gas can be mixed in all proportions with the normal sendout gas.

All of this work is of more than idle interest to the petroleum industry, allied as it is with the gas industry and interested as it is in the relief of fuel shortages in other fields which complicate its problems in times of its own heavy loads. Moreover, the fact that heavier hydrocarbons can be catalytically reformed with steam to yield the "carrier gas" for propane and butane will make the petroleum industry at least the supplier of raw materials for plants that may use this process.

Petrochemical Economics and High Petroleum Prices

AS has been commented upon many times in this feature and elsewhere, the economics of petrochemical production are complex indeed, and vary considerably from case to case and company to company. They also vary between the chemical-industry producer and the petroleum-industry producer. By the former, petroleum materials must be considered in the same light as other basic materials—on the basis of cost, supply, purity, etc. For the petroleum-industry chemical producer, however, the basic petroleum fractions have a dual function—they can either be used for the production of chemicals or enter the overall fuel picture.

Two recent statements[2], [3] serve to show the different viewpoints engendered by the recent sizable rise in petroleum prices. From one of these, an editorial feature in *Chemical Industries*[2], may be judged the chemical industry's viewpoint on "ballooning costs of raw materials, freight, and labor," which "have made a hollow whisper of one of the (chemical) industry's favorite talking points—continually decreasing prices.

"The vigorous young petrochemicals industry has been a major factor in bringing chemicals to postwar markets. * * * However, petrochemicals have their difficulties. With the possible exception of methane and ethane, raw materials can no longer be had at give-away prices (*by the chemical industry*). Even where natural gas (methane) is the desired raw material, chemical companies are faced with the necessity of buying up whole gas fields to insure continuity of supply for a sufficient time to amortize investment.

"The increase in the price of crude oil is forcing refiners (!) to leave nothing in the bottom of the oil barrel, and fewer hydrocarbons will be sold in other forms than fuel. This trend will continue since the refiners' primary job is selling energy, not chemicals."

From a petroleum industry viewpoint, all this is only partially true. The alert, informed refiner will not ignore for long a high olefin content in effluent gases from certain of his plants, even if these gases are economic for use as refinery fuels without regard to their constitution. In this case, it is true, he may balance chemicals production against fuel synthesis by polymerization, and will often choose the latter for numerous reasons, but this does not mean that he will give no attention to chemicals production. In the past, it is true, many petroleum refining by-products were valued at little or nothing—sometimes not even at fuel equivalent values. This situation no longer exists, except in isolated instances, but "the refiner's primary job" is not simply "selling energy"—it is selling products for maximum return in a highly competitive field, and that means giving constant attention to new uses for product materials.

As the editors of PETROLEUM PROCESSING recently pointed out[3], "the

(1) Anon., "Tomorrow in Petroleum Technology," PETROLEUM PROCESSING 3, No. 7, 628 (1948).

(2) Anon., "What's New—Twenty Ought and Six," *Chemical Industries* 63, No. 2, 209 (1948).

(3) Anon., "Editorial Viewpoints—The Cost of Natural Gas vs. Petrochemicals Manufacture," PETROLEUM PROCESSING 3, No. 7, 712 (1948).

cost of the gas is (frequently) a small factor in the cost of the many petrochemicals made in relatively small volume from natural gas, and even further advances in the price of raw material would (in many cases) have little effect on the total cost of the product.

"Increases in the cost of the raw materials for chemical manufacturing from petroleum sources, whether natural gases or refinery gases, would seem to place the oil companies in a more favorable economic position than today as regards the manufacture of chemicals. The oil company, and to a certain extent the natural gasoline manufacturer, has a choice over its raw material for chemicals that the outside manufacturer is often denied. They can dovetail their operations in this field with their manufacture of volume products as economic conditions warrant. Also, it is possible that the growing domestic fuel market may keep the price of natural gas high, while market conditions may bring the cost of refinery gases and propane to a point where they give a distinct economic advantage to the oil company or other manufacturer using them as raw material for chemicals."

All of this does not mean that the petroleum industry is not fully aware of the impact of the increase in price of its materials on the petrochemicals field, within both the petroleum and chemical industries. The need for careful analysis of each proposed excursion into this field has thereby been intensified, and there is no doubt that many projects which would have been economic a few years back will no longer prove sound future investments. However, there is no reason to believe that present high petroleum prices will do more than slow the trend toward increasing chemical use of petroleum materials—they will most certainly not stop it.

Stanolind's Cancellation Of Synthine Plant

MUCH HAS ALREADY BEEN SAID elsewhere about Stanolind's "shelving" of plans for its multi-million dollar Synthine plant, intended for erection at Garden City, Kansas. The reasons given for this action—rising costs of equipment and delays in getting materials—are valid ones for any private enterprise, whose actions must be governed by the profit motive. The soundness of the process was not questioned, and hope was expressed that further Synthine research plus a stabilizing of equipment costs might make it possible to revive the project two or three years hence; Stanolind is retaining the plant site.

From a private industry rather than Government industry viewpoint, however, this apparently necessary cancellation may have unfortunate repercussions. The petroleum industry has never pretended that this Garden City project plus the smaller Brownsville, Texas, plant (which will be completed) could supply the nation with any significant amount of synthetic fuels in an emergency, but plans for both plants served as visible tokens of the industry's ability to stand on its own feet in regard to building synthetic fuels plants, and a refutation that there was any need for the Government to build plants simply to make certain that some were erected. Other arguments against Government entry into competition with private industry are still valid, but they are much weakened by this event.

If the economics on which Stanolind's decision were based are universally applicable, it would certainly appear that the petroleum industry is in no financial position to construct a large-scale synthetic fuels industry in the immediate future. The need for such an industry, of course, is highly debatable, but the decision to erect one may come from politicians and military circles.

The Synthine (Fischer-Tropsch) process is the only large-scale synthetic fuels process which has shown economic potentialities for competition with petroleum. This set-back does not lessen the merit of the process—it simply indicates that the time may not yet be ripe for its large-scale competitive use, and it highlights the need for the continued research efforts being displayed in petroleum industry and Government laboratories.

This process will certainly be employed on a large scale if a Government-legislated program should come into being. In the intervening months between now and the next session of Congress, the petroleum industry will do well to marshal its arguments for leaving the construction of a synthetic fuels industry in private hands, since it is highly likely that, sooner or later, such an industry will actually be needed. However, if national security is actually at stake—or appears to be, in the eyes of those in Washington who will decide the matter—the petroleum industry should certainly be prepared to campaign vigorously for the erection of such an industry in such a manner that it will not eventually lead to Government control of the entire petroleum industry.

Cancellation of the Stanolind Synthine plant, in itself, is a small matter commercially, but it may be seized upon as a sign of petroleum industry weakness, which it certainly is not.

Oxo Process Receiving Commercial Attention

AS REPORTED LAST YEAR in this series, the "Oxo" process for synthesizing aldehydes and alcohols (and their derivatives) from carbon monoxide, hydrogen, and olefins is receiving much attention in this country. According to one source(4), the Esso Standard Oil Company is already operating a plant at Baton Rouge, La., using this method for the synthesis of isooctyl alcohol, and the Standard Oil Co. (Ind.) is said to be planning to produce nonyl alcohol ("said to be about 75% 3,5,5-trimethyl-1-hexanol") at its Whiting, Ind., refinery, early next year.

This same source(4) reports that the Oronite Chemical Co., The Texas Co., and du Pont are also interested in using the Oxo process for the synthesis of high-molecular-weight alcohols. Du Pont may be in production by mid-fall; Shell will probably first use the process in a huge petrochemicals plant under construction in England.

Coincidental to the commercial interest in this process is the publication by the Bureau of Mines of a critical review(5) of its chemistry and reaction mechanisms.

Commercial interest in the United States, at present, is centered around the production of C_8-C_9 alcohols for use in the synthesis of plasticizers (phthalic and maleic acid esters, chiefly). In Germany, however, the chief use was the sulfonation of the alcohols produced to yield detergents. Plasticizers were also produced there, and some of the alcohols were actually oxidized to yield fatty acids. Other products included cutting oils, lubricating oils, hydraulic fluids, synthetic drying oils, synthetic essential oils, etc. The Diesel oil produced "by converting a range of Oxo alcohols to their nitric acid esters" had the "astonishing cetene number of 280."(5) Moreover, "a substantial increase in the octane number of gasoline results from the Oxo reaction on the double bond content of the gasoline and subsequent hydrogenation";(4) this produces increased branching.

Whether it is used by the petroleum and chemical industries solely as a method of synthesizing chemicals, or whether it is actually applied to the improvement or synthesis of "petroleum products," the Oxo process has an interesting future ahead of it.

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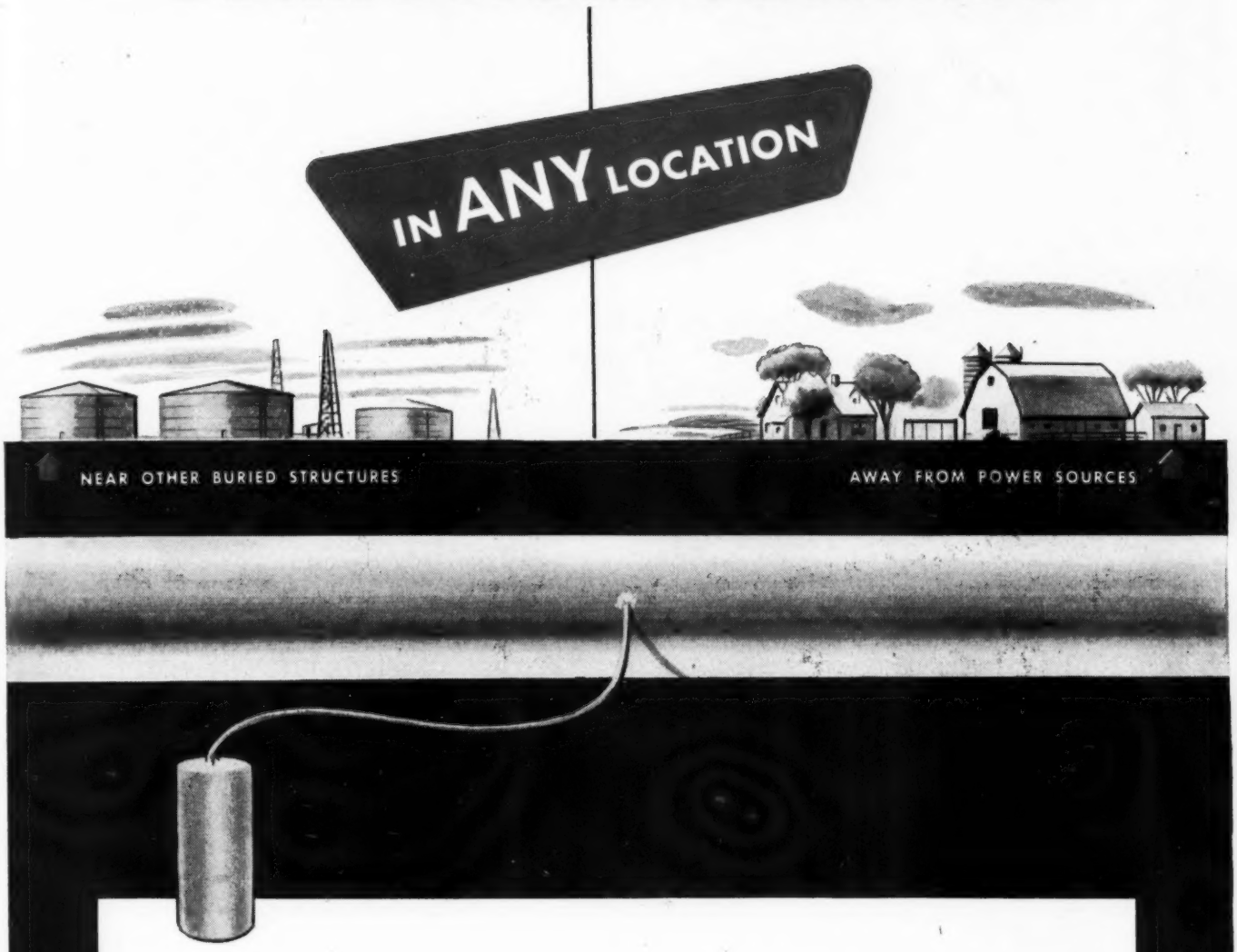
(4) Anon., "What's New—'Oxo-ated' Olefins," *Chemical Industries* 63, No. 2, 211-12 (1948).

(5) Wender, I. and Orchin, M., *Critical Review of Chemist of Oxo Synthesis for Production of Alcohols from Olefins, Carbon Monoxide, and Hydrogen*, U. S. Department of the Interior, Bureau of Mines Report of Investigations 4240, Pittsburgh, 1948, 26 pages.

CORROSION CONTROL



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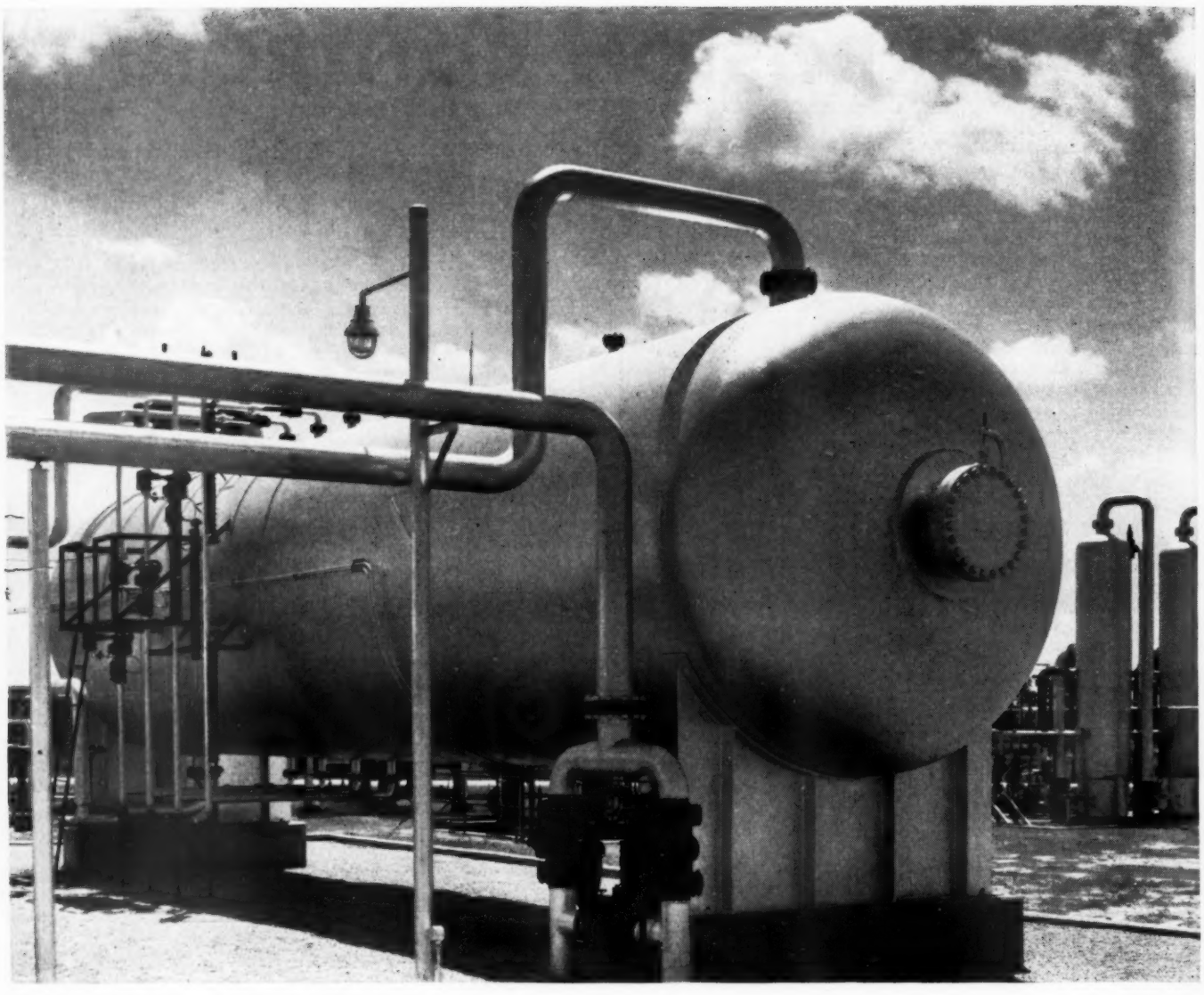

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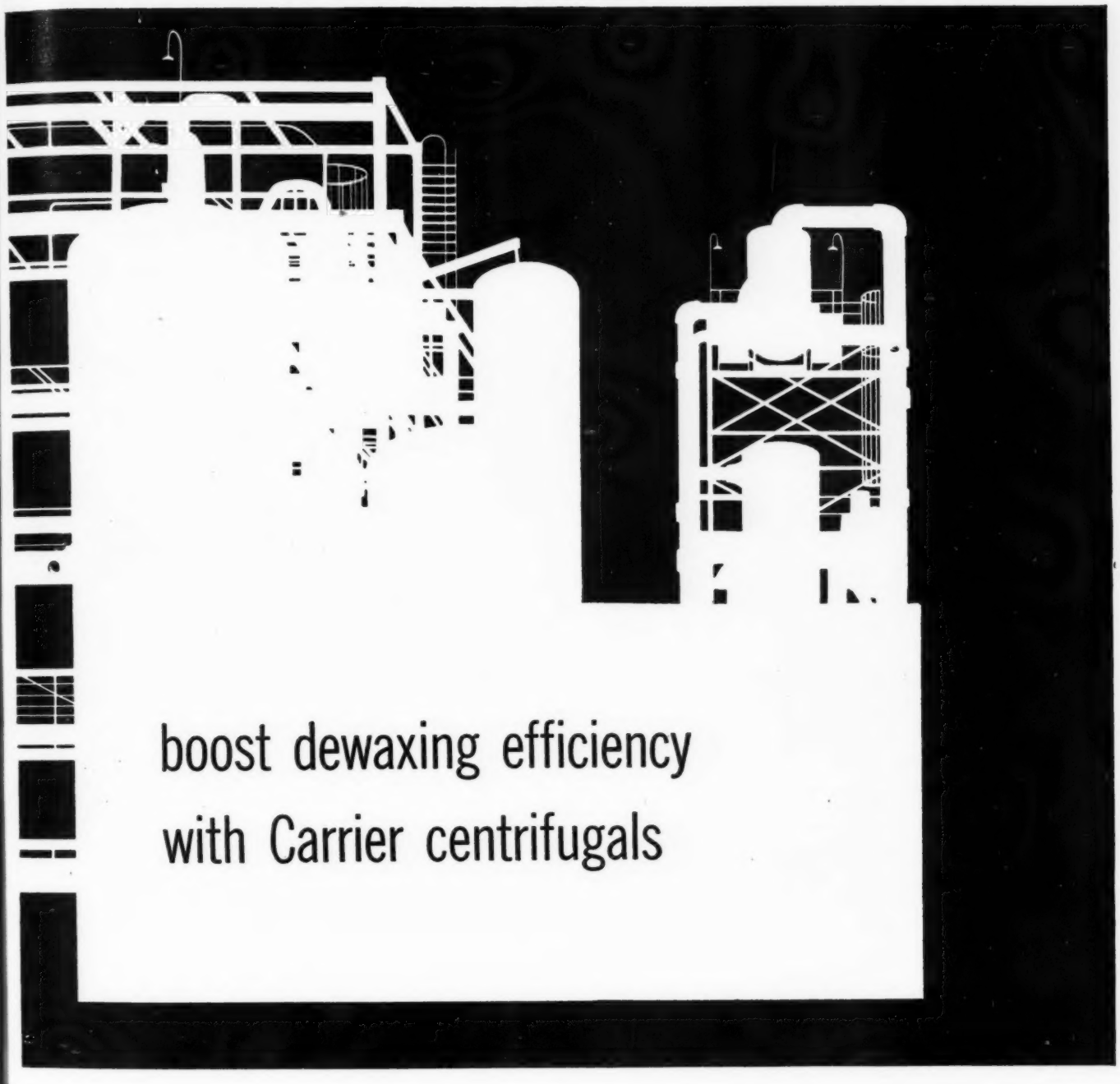

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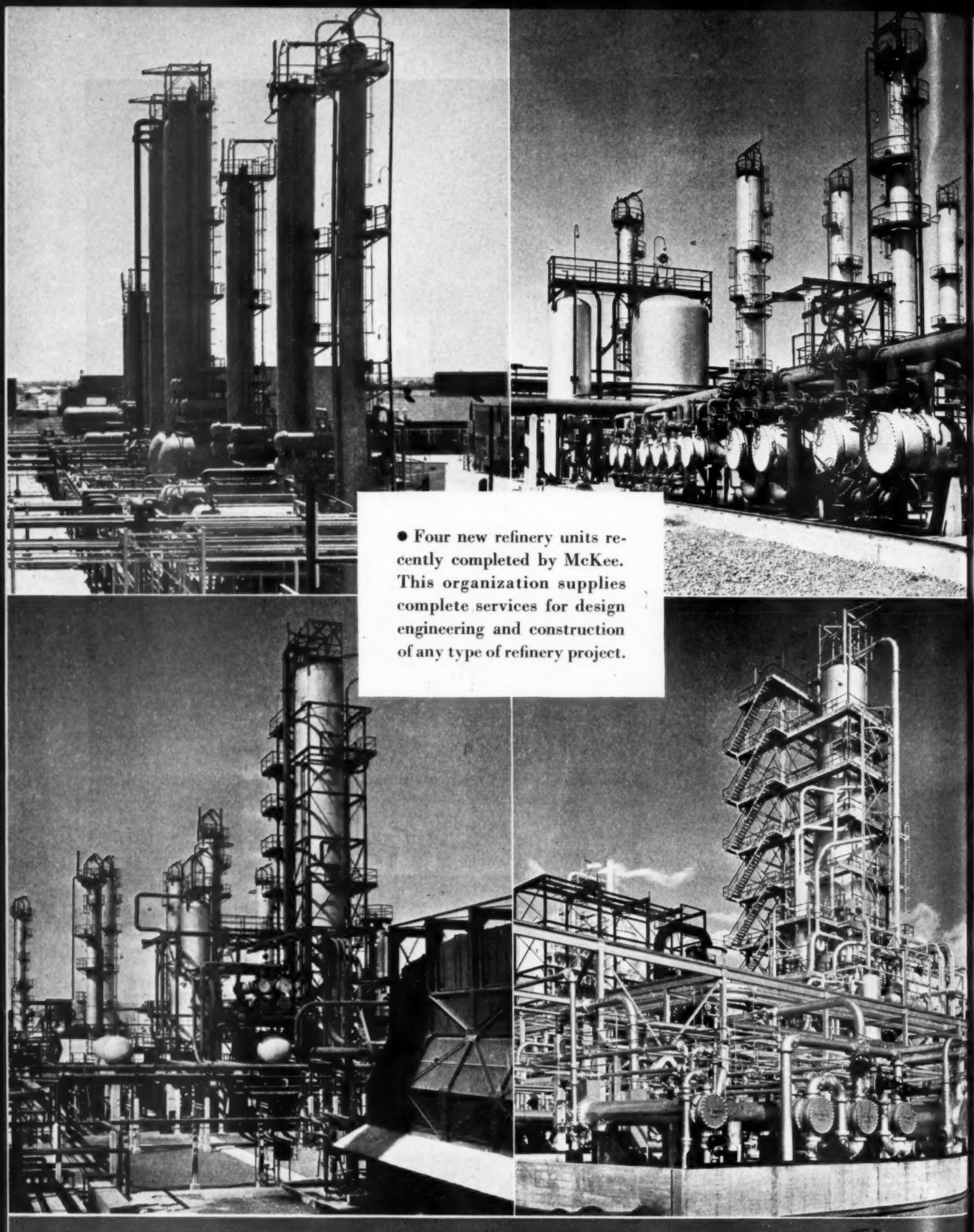

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PETROLEUM PROCESSING

OCTOBER, 1948

And Now–

GLYCERINE from PETROLEUM

By D. P. THORNTON, Jr.
Assistant Editor

HOUSTON—The first tank car of commercial synthetic glycerine, 99% pure, left here on the end of a freight train Sept. 16, highlighting dedication ceremonies earlier in the day at Shell Chemical Corp.'s Houston works, where the first glycerine plant ever built had just gone on stream. Present for the ceremonies were more than 100 representatives of Shell Oil Co., Shell Chemical Corp. and numerous invited guests.

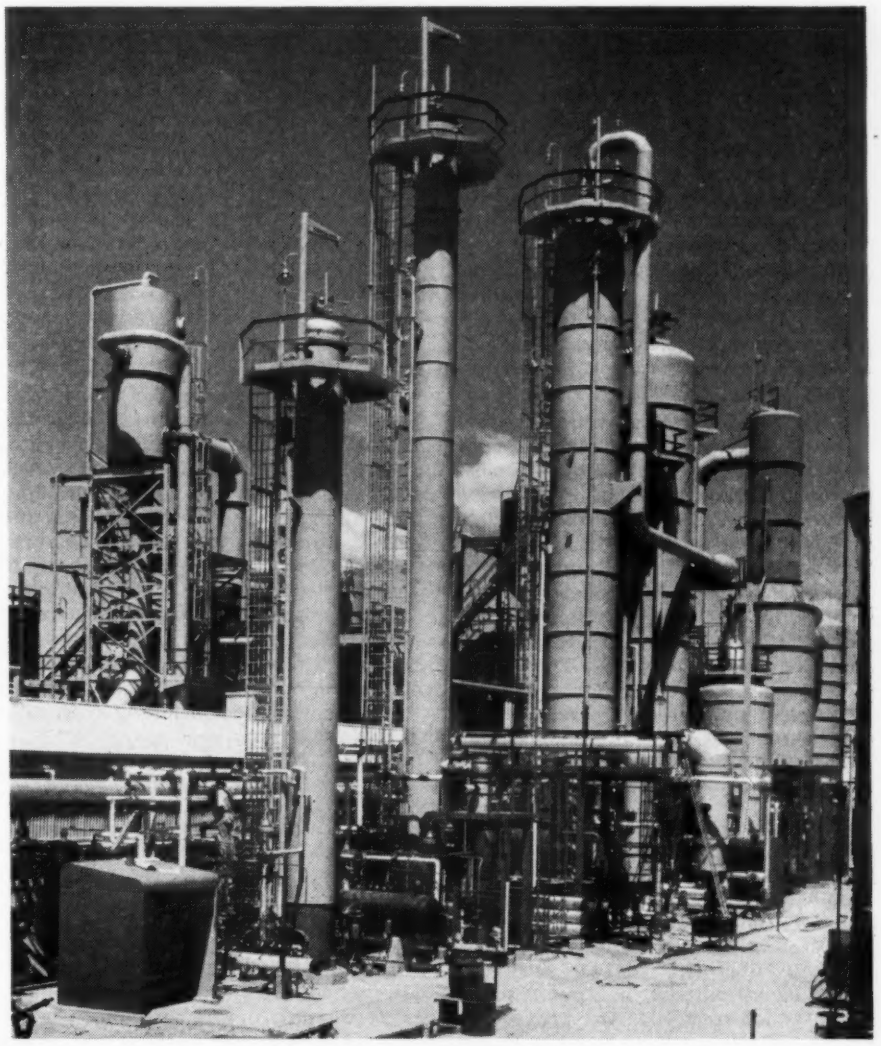
Synthetic glycerine long has been attempted by chemists, to relieve the shortage of the natural product and to make possible a higher purity material (by control of unwanted components) than is practical with that obtained from natural glycerides. Glycerine supplies in the past have been deficient because of production shortages of natural fats, and as a result of increased industrial demand in recent years for glycerine to be used in the manufacture of resins, paints, cellophane, explosives, cosmetics and drugs, as well as to maintain moisture in foodstuffs and tobacco. Another difficulty has been the fact that glycerine heretofore always has been a by-product of the soap and fatty acid industries, and as such remained dependent on the primary product of these industries.

Germans Used Fermentation

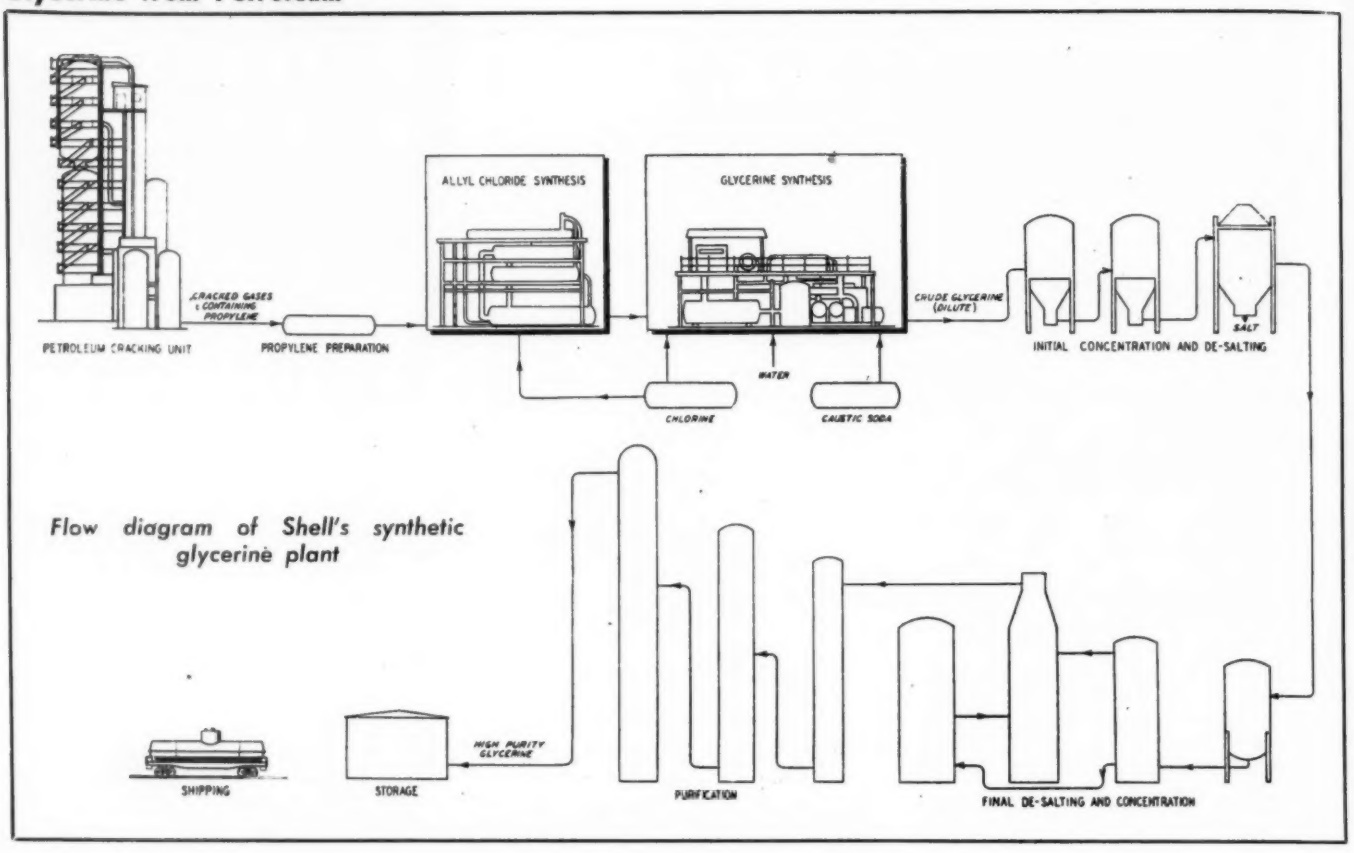
One scheme was to achieve glycerine production through fermentation, since Pasteur had demonstrated that a small amount was formed during the fermentation of molasses to the principal product, ethyl alcohol. Although the method is technically feasible, indeed the Germans are reported to have achieved production of 13,000 tons annually during World War I, it has never received wide acceptance.

From the chemical standpoint there were several possible methods of making glycerine in the laboratory. However, the principal catch to them all was that the starting materials themselves are relatively difficult to synthesize, or the intermediate steps to glycerine are numerous, complicated, or both. Consequently, except in times of critical shortage of the natural glycerine, chemical synthesis could not be economically competitive, and hence there was no incentive to build the necessary facilities.

These facts piqued the interest of Shell Development Co. scientists and prompted an investigation into the possibilities of producing it from refinery "waste" gases, particularly those containing three carbon atoms. The present $8,000,000 plant, construction of which started in September, 1947, is the culmination of more than 20 years of laboratory and pilot plant development. The immediate anticipated result will be a relative stabilizing of the price of glycerine, which in past years has ranged from



General view of the recovery and purification section of Shell Chemical Corp.'s new $8,000,000 synthetic glycerine plant at Houston, which was dedicated and put in operation Sept. 16



Flow diagram of Shell's synthetic glycerine plant

a few cents to $1 per lb., with the present price being about 40c.

Aside from the fact that the glycerine plant depends on a unique chemical synthesis step—the substitution of chlorine into a propylene molecule without destroying the double bond, until a few years ago regarded as a technical impossibility—the processing represented is important because it insures this country from future shortages of this material.

Shell Chemical representatives believe it will serve to stabilize not only price but production of glycerine generally. Its capacity of 50 tons daily represents between 15 and 20% of the previous total U. S. production of 200,000,000 lbs. annually. A replica could be built under wartime conditions, according to Jan Oostermeyer, Shell Chemical president, in from 12 to 14 months. Thus this, and other potential plants, can and will render us more independent than ever before of natural production—and housewives can quit saving kitchen fats.

At the present time, no more synthetic plants are planned. This is in part dictated by Shell's desire to run this one long enough to determine if process or equipment changes are desirable and to establish dependable operating data. Although protected by patents, it is not at present intended to license the process to others. In the event of wartime, however, Shell will make its know-how available when and if needed. A large part of expected plant production is contracted for at current market prices, f.o.b. plant, over the next several years.

Production costs have not been accurately determined except from pilot plant data. It is stated by Oostermeyer, however, that operating costs will be a relatively small part of the total manufacturing cost. Principal items will be raw materials—propylene, caustic soda and chlorine—and amortization of investment.

It has been known for many years that glycerine could be synthesized from numerous organic compounds, but always there was difficulty from the commercial standpoint in finding a procedure whereby the product could be made and sold at a price comparable with production from natural glycerides. Not until Shell Development scientists refused to believe the textbooks and found the present unique route through substitutive chlorination of propylene did a commercial synthesis look feasible.

Shell's research indicated there were several promising routes—providing they could chlorinate propylene *without* destroying the latter's chemical structure. They set about learning how to prepare allyl chloride, $CH_2=CH-CH_2Cl$, from propylene $CH_2=CH-CH_3$.

Past knowledge indicated this probably was impossible; the chlorine simply would add itself to the molecule by destroying the double bond, producing propylene dichloride ($CH_2Cl-CHCl-CH_3$). This was useless as an intermediate in synthesizing glycerine ($CH_2OH-CHOH-CH_2OH$), unless a third chlorine atom could be persuaded to attach itself to the remaining carbon atom—a difficult step.

Success eventually was achieved by carefully controlling reaction conditions — temperature, pressure, ratio of propylene to chlorine, mixture conditions and purity of the raw materials. High yields were obtained, which were confirmed in pilot plant work and, now, in commercial operations.

No details on actual reaction conditions in the present commercial process, either in the new glycerol plant or in the separate plants producing allyl chloride or allyl alcohol, have been released by Shell Chemical. The process description which follows is taken from the excellent account of pilot plant work on the glycerol synthesis project, reported by E. C. Williams before the American Institute of Chemical Engineers in December, 1940 (*Transactions,* 37, 157-207, 1941), and from other scattered sources.

Propylene, for instance, must be 98% pure or better. It was found that the presence of propane, particularly, would complicate the reaction, since it likewise would be chlorinated. Propane chlorinates not only are difficult to separate from allyl chloride, but an appreciable amount of chlorine would be wasted in an unwanted reaction.

Mixing of the reactants before preheating to reaction temperature, or preheating both separately and then mixing, likewise was undesirable.

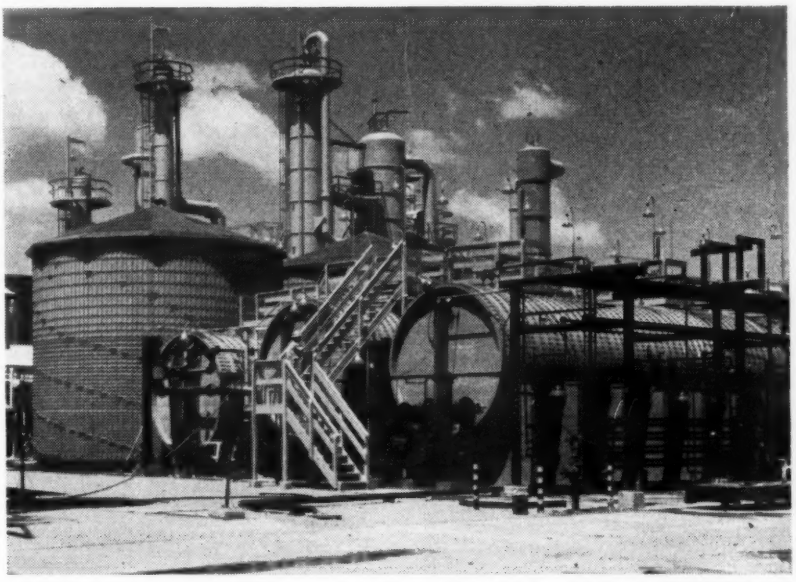
The former led to unwanted side-reactions and carbon formation. The latter produced uncontrollable reactions, even to flames and explosions. The solution to this once-serious difficulty was found in preheating only the propylene to 750° F. before mixing with the chlorine stream. A mixing jet was used, wherein the propylene entered the chlorine stream through two opposed side tubes which injected it at right angles to the flow.

Reaction Is Exothermic

Heat of reaction, it was found, would promptly increase the temperature in the reactor proper, which is maintained in the range 930 to 980° F. for optimum yields. Pressures are not controlling but should be held constant; they may range from atmospheric to 150 or 200 psi. Residence time in the reactor likewise is not critical, providing sufficient time is allowed for the reaction to go to completion. Propylene always should be in excess of chlorine, with yields ranging from 60 to 80% of theoretical as the ratios are increased from 3 to 5. Recovery system costs would make higher ratios impractical.

Vapors leaving the reactor include unreacted propylene, allyl chloride, up to 10% of the yield based on chlorine in the form of both unsaturated and saturated hydrocarbon

THIS MONTH'S COVER PICTURE



Shown on the cover this month is a closeup view of the dilute glycerine synthesis unit at Shell's Houston plant. The horizontal wooden tanks, 60 ft. long and 13 ft. in diameter, are mixing vessels, with wood being used for corrosion resistance and to avoid impurities in the reaction mixture. Principal raw materials in Shell's glycerine synthesis process are allyl chloride, chlorine and caustic soda. In the background are the vacuum concentration and distillation towers used in the preparation of purified finished glycerine. These towers are fabricated of nickel clad steel, again for corrosion resistance and to prevent contamination

POSSIBLE STEPS IN THE SYNTHESIS OF GLYCERINE

(1)—THROUGH ALLYL CHLORIDE:

(a) $CH_2{=}CH{-}CH_2Cl + NaOH \rightarrow CH_2{=}CH{-}CH_2OH + NaCl$
(allyl chloride) (allyl alcohol)

(b) $3CH_2{=}CH{-}CH_2OH \xrightarrow{+\,Cl_2} CH_2Cl{-}CHCl{-}CH_2OH \rightarrow CH_2(OH){-}CH(Cl){-}CH_2(OH)$ (glyceryl chlorohydrins) $\xrightarrow{+\,3NaOH,\ (5\%\ solution)} 3CH_2(OH){-}CH(OH){-}CH_2(OH) + 3NaCl$ (glycerine)

(glyceryl chlorohydrins) $\xleftarrow{+\,2HOCl} CH_2(OH){-}CH(OH){-}CH_2Cl$

(2)—THROUGH DIRECT CHLOROHYDRINATION:

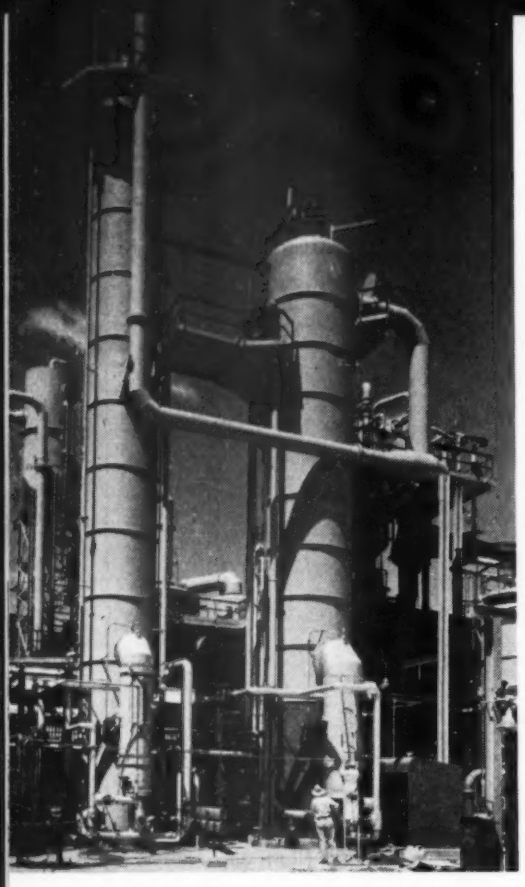
$2CH_2{=}CH{-}CH_2Cl + 2HOCl \rightarrow CH_2(Cl){-}CH(OH){-}CH_2Cl$ (glyceryl dichlorohydrins) $\xrightarrow{+\,4NaOH} 2CH_2(OH){-}CH(OH){-}CH_2(OH) + 4NaCl$

(glyceryl dichlorohydrins) $\rightarrow CH_2(OH){-}CH(Cl){-}CH_2Cl$

(3)—CONVERSION TO AN EPICHLOROHYDRIN:

(a) $2CH_2(Cl){-}CH(Cl){-}CH_2(OH) + Ca(OH)_2 \xrightarrow{(distill)} 2CH_2(Cl){-}CH(-O-){-}CH_2 + CaCl_2 + 2H_2O$
(dichlorohydrin) (epichlorohydrin)

(b) $CH_2(Cl){-}CH(-O-){-}CH_2 + NaOH + H_2O \rightarrow CH_2(OH){-}CH(OH){-}CH_2(OH) + NaCl$
(glycerine)



Closeup view of a portion of the glycerine recovery and purification towers

dichlorides, hydrogen chloride and a small quantity of high boiling hydrocarbon chlorides.

Hydrogen chloride is scrubbed out with water, or may be picked up in hydrochloric acid for conventional recovery. Allyl chloride is absorbed from the vapor stream in any convenient solvent; kerosine was used in pilot plant investigations. This material then is stripped from the kerosine and freed of impurities by distillation. Propylene is taken overhead, followed by the mono- and dichloropropenes, leaving an ultimate residue of high boiling hydrocarbon chlorides.

Once allyl chloride is secured, the preferred routes to glycerine either are hydrolysis to allyl alcohol, followed by chlorohydrination and final hydrolysis, or direct chlorohydrination and final hydrolysis. The chemical reactions involved in these two routes are described in the box on page 933.

A third possible route can be used, starting with the dichlorohydrins produced by either of the principal reactions in the first two routes (possible side reactions are not indicated for simplicity.) This converts them to an epichlorohydrin, which subsequently may be hydrolyzed to glycerine as shown in Reaction 3. It also may be condensed with phenol-type compounds to form resins useful in paints and varnishes as film-formers.

Williams describes the alcohol route pilot plant operation as reacting the allyl chloride with a 5% solution of caustic soda (NaOH) under conditions of approximately 320° F. and 200 psi. Control of alkalinity is extremely important as well as reaction temperature and other variables. Sodium carbonate may be used instead of caustic soda, injecting caustic soda solution to keep pH within the desired range. Reaction will go forward solely with the carbonate, but evolution of carbon dioxide results in high pressures. If vented, the CO_2 will carry volatile hydrocarbon compounds with it, necessitating expensive recovery operations.

The chlorohydrin reaction, as shown in Reaction 2, may be carried out by the use of either gaseous chlorine or, if its presence in the equipment is undesirable, with hypochlorous acid. Williams reported the use of a packed tower reactor kept full of chlorine, over which the alcohol (or the chloride in Reaction 2) is trickled.

The unreacted solution then is mixed with an aqueous solution consisting of 10% NaOH and 3% Na_2CO_3 and transferred to a stirred, heated reactor. In order to render the process continuous, avoiding long residence times in the reactor, the reactor is kept liquid full, sufficient withdrawal of reaction mixture being made to allow for the desired feed rate. The reaction is allowed to complete itself in a second vessel, heated but unstirred. Effluent from this "soaker" is neutralized with HCl.

From this effluent the allyl chloride (or alcohol) is stripped for recycling, cooled for temperature control and recharged to reactor feed. Purification steps consist of neutralization with hydrochloric acid, concentrating the weak solution through multiple-effect evaporators, filtration to remove the solid salt, and final vacuum distillation of the glycerine to desired specifications.

Commercial Production

As previously stated, the exact steps in the commercial unit just placed on-stream at Houston have not been made public. There actually are three separate and complete plants, all making use of essential portions of the various routes just discussed in an undisclosed manner. One makes allyl chloride and allyl alcohol from propylene; another makes glycerine, and the third, epichlorohydrin.

Commercially, allyl chloride is first synthesized at the glycerine plant from carefully purified propylene by chlorination at high temperatures, according to information released at the dedication. This material then is carefully purified through a series of distillation and absorption steps, similar to that used in the allyl chloride unit which has been in operation for some time.

The pure allyl chloride then is reacted in a continuous process with caustic soda and chlorine to produce a week solution of glycerine, salt and water. Temperatures here are said to be in the range of 100-400° F. and pressures can vary from atmospheric to 150 psi.

Subsequent steps consist of a concentration in evaporators to produce a concentrated salt-glycerine slurry. Salt is principally separated in a settling tank at this point. Further vacuum evaporation continues until the product is substantially freed of salt, whence a series of vacuum distillations completes the treatment.

Various corrosion-resistant alloys, including Hastelloy, are used throughout the plant to minimize corrosion as well as to avoid contaminating the product. Specially lined storage tanks are used, and the product is shipped in aluminum tank cars, insulated externally with glass fibers.

The unit is rated at 50 tons daily of product of 99% purity or better, although it will make glycerine meeting all commercial specifications for grades ranging from 95 to 99.5%, including pharmaceutical grades. Product of 99.7% purity already has been produced on the commercial unit during initial operations.

Raw Materials Next Door

Raw materials are received from Shell Oil Co.'s nearby refinery, and from the adjacent plant of Diamond Alkali Co., which produces chlorine and caustic soda electrolytically from salt found in a salt dome just across the Houston Ship Channel. One of the principal byproducts of the glycerine plant, common table salt, is used in further synthesis operations elsewhere in the plant.

Hydrogen chloride, another by-product, is purified and concentrated in an entirely separate unit in the chemical plant, and likewise is used in other syntheses. Trichloropropane, a by-product from both the glycerine and epichlorohydrin units, similarly is processed elsewhere in the plant and is usable directly as a solvent.

All told, there are 16 separate chemical units at present comprising the Houston plant of Shell Chemical. These are: isopropyl alcohol, acetone, epichlorohydrin, glycerol dichlorohydrin, trichloropropane, diallyl phthalate, methyl isobutyl ketone (two units), methyl isobutyl carbinol, allyl chloride, D-D, allyl alcohol, secondary butyl alcohol, methyl ethyl ketone (MEK), ethyl alcohol and glycerine. Now under construction is a hexylene glycol plant, and a second ethyl chloride plant is expected to be completed before year's end. Total plant site comprises approximately 240 acres, of which about 40 are used for processing units, another 40 for storage and general facilities and the balance, to the east and northeast, is being held for future expansion.

ISA Meeting and Exhibit Indicates Trend Toward Precision, Efficiency, Versatility

A STAFF REPORT
by the Editors of
Petroleum Processing

Simplified "push-button" control panels with fewer instruments to watch.

Improved accuracy in existing control instrument design.

New principle of operation for a flow meter.

New applications for conventional instruments.

Increased versatility and flexibility in recorders.

Trends toward standardized instalation procedures and repair parts.

These were some of the facts evident in the meeting rooms and on the exposition floor at Convention Hall, Philadelphia, Sept. 13-17, when nearly 15,000 engineers, technologists and scientists attended the Instrument Society of America's Third National Instrument Conference and Exhibit. Among a total of 39 papers given at the technical sessions of this 1948 meeting, the following points of interest to the petroleum processing industry were brought out:

1—Substantial savings in fuel in the boiler plant of one refinery were realized through the use of a controller arrangement incorporating a continuous oxygen analyzer in the fluid gas stream.

2—It is possible to streamline the operation of refinery process units such as crackers and the like with a simplified control console utilizing as few as three recorders and a set of push-button switches for quickly readjusting control points at critical locations in the flow stream when upsets occur.

3—Use of interconnected (cascade) instrumentation by another refiner was demonstrated to minimize the effect of sudden load changes in the controlled fluid stream of a fractionator.

4—Although much investigation is still needed on valve characteristics and their effect on process control, a number of instrument manufacturers were able to suggest proper calibration procedures under certain limited conditions of flow.

5—Data were presented to show the effect of lag in pneumatic transmission systems due to long stretches of tubing in three different diameters and in lengths up to 2000 ft.

6—Considerable thought and care must go into the planning and administration of an instrument engineering department and an instrument training program.

7—A new method and apparatus have been developed for the measurement of particle-size of sub-sieve powders. Similar to the Roller elutriator technique, it uses gaseous rather than liquid sedimentation to achieve good reproducibility down to the one micron size and saves time in analysis.

Editorial staff reviews of a number of these papers appear in this issue of PETROLEUM PROCESSING, beginning on page 945.

New Instruments Exhibited

Although the meeting rooms were filled to overflowing at most of the technical sessions, visitors at Convention Hall found many fascinating new devices commanding their attention on the exposition floor. Among such products were:

1—A flowmeter of improved accuracy based on the stroboscope principle.

2—A multiple point, potentiometric temperature recorder of the strip tvpe which can handle up to 140 thermocouples. It will go through a complete cycle recording temperatures for all the couples in less than 10 minutes, at the rate of one every four seconds.

3—A circular type recorder for any type of condition—flow, pressure, temperature, liquid level, etc.—which can handle with one pen arm up to six different readings from as many different locations in a process.

4—A small console type remote control instrument panel which can be substituted economically for the usual large control rooms ordinarily associated with complex refinery units.

5—A mercury manometer of 1500 psi. working pressure said to offer accuracy and long service life and wide adaptability through interchangeable range chambers.

6—A 15,000 psi. diaphragm-motor operated control valve employing a plastic seal with good lubricating properties to provide for ease of operation at any fluid pressure.

A number of other new instruments displayed at this Exhibit have already been described in the September PETROLEUM PROCESSING "What's New!" section. Others will be reviewed in future issues as manufacturers are able to supply greater details and illustrations. Just as in previous National Instrument Exhibits, several manufacturers showed devices still in the development stage so that they could obtain first-hand reactions, criticisms, and suggestions from the men who would ultimately put the instruments to use.

Flowmeter Uses Stroboscope

The flowmeter employing the stroboscope principle of operation is called a "Stroboflow" and is based upon the premise that the volume of fluid delivered by a pipe in a given time is the product of the cross-sectional area of the pipe and the velocity of the flowing fluid. If these two factors are maintained, changes in temperature, in gravity, in pressure, or in viscosity will have no effect on the volume of the flow.

This new instrument utilizes a nozzle of carefully designed dimensions in which the velocity of the fluid will always bear a linear relationship to the total volume of flow per unit time. Combined with this nozzle is a rotor, or impeller, which engages the fluid passing through the nozzle much as a pinion gear engages the teeth of a rack. In a properly constructed housing, the rotational speed of the rotor will always bear a linear relationship to the velocity of the fluid in the nozzle. This relationship remains linear over a range of speeds which may vary from 100 to several thousand revolutions per minute.

In the instrument, a window is provided on both sides of the impeller housing. Rotational speed is measured by means of a stroboscope, with the indicator calibrated in the units desired. At its present state of development, the device has a range of about 100 cc. to 20 gal./min. with an accuracy of 0.01 to 0.02%, and has been designed primarily for use in the laboratory. However, the manufacturer believes it will find many industrial applications with no loss of precision.

Multiple Recorder Changes Pens

The new "Multi-Record Dynalog" is the equivalent of six separate instruments. Using one measuring circuit, and one pen-arm assembly, it will record up to six measurements on a single circular chart. The measuring circuit is connected to each of

six successive points of measurement through a cam-operated switching arrangement, driven by a constant-speed motor.

A small turntable carrying six inking pens with various colored inks and operated synchronously with the switching mechanism feeds a new pen to a magnetic grab at the end of the pen arm every six seconds. After the ink impression has been made on the circular chart, the pen arm returns the pen to the turntable and picks up the next successive color, and the cycle is repeated. The instrument can be used for temperature, flow, pressure, level, etc., but only for one type of measurement per instrument.

The small console type control panel with few recording instruments and remote control methods for handling upsets and the like was designed to substitute for the conventional control houses on refinery units. Using a "Remoteset" instrument the operator can vary control ranges at various critical points in the process. A more complete description of the instrument will be found in the review of the paper, "Supervisory Control Systems" by Gess & Hutchinson, on page 948 of this issue.

Push Standardization Program

With the validation for publication of two recommended practices, steady progress is becoming increasingly evident in the ISA program of standardization, James G. Kerley, Shell Oil Co., New York, and chairman of the ISA Recommended Practices Committee, told PETROLEUM PROCESSING. The two practices adopted follow:

R. P. 1, on thermocouples and thermocouple extension wire, covers symbols for types of thermocouples and extension wires, and a color code for thermocouple extension wires, and a color code for duplex insulated thermocouple wire. It is felt that if suppliers will conform to this recommended practice, it will result in eliminating much of the present confusion from the wide variety of color codes for identifying wire composition, etc. The work on R. P. 1 was handled by a sub-committee headed by H. H. McCarthy, Standard Oil Development Co., as chairman.

R. P. 2, on manometer tables, presents in some 60 pages of information standard tables covering densities, temperature coefficients, and pressure values for the fluids most commonly used as manometer fluids. In addition, terms and constants are defined, and a set of conversion factors and tables are given for various classes of manometers. W. G. Brombacher, National Bureau of Standards, is chairman of the sub-committee which handled this work.

Ten other sub-committees are also undertaking studies in this program, some of which have been established only recently and others of which are close to completion.

The sub-committee on flowmeter installation practices (chairman, J. Johnson, Jr., E. I. du Pont de Nemours & Co., Wilmington) is working on R. P. 3. Its current investigation is on seal pots and condensation chambers. Future activities are contemplated on flowmeter arrangement and manifolding.

The sub-committee on control valve and by-pass manifold installations (chairman, William H. Fortney, Humble Oil & Refining Co., Baytown) is concerned with R. P. 4, the chief aim of which is systematized manifolds that can be fabricated quickly from stock parts readily available in the instrument shop.

Surveys 300 Engineers

The sub-committee on instrumentation flow plan symbols (chairman, David E. Hostedler, Foster-Wheeler Corp.) has R. P. 5 as its project. This group has surveyed about 300 engineers in various industries, and expects to arrive at a set of standard symbols for instruments which will save considerable drafting time.

Mr. Kerley anticipates early adoption and validation of Recommended Practices 4 and 5, perhaps by spring of 1949.

R. P. 6 is the undertaking of the sub-committee on pneumatic transmitter and controller usage (chairman, Harry F. Moore, Standard Oil Development Co.). The committee's goal is standard pressure ranges for pneumatic telemetering systems and uniform controller pressure ranges. One of its current studies is in regard to trouble-free instrument air supply systems.

Somewhat allied to the Moore committee is the sub-committee on pneumatic circuit pressure tests (chairman, S. C. Chapman, Lago Oil & Refining Co., Aruba Refinery, Netherlands West Indies). It is working on R. P. 7, which will offer simplified procedures for detecting leaks in pneumatic systems, and will attempt to eliminate some of the more troublesome and hazardous methods reported in use today.

The sub-committee on outside instrument protective cabinets (chairman, W. A. Crawford, du Pont), and the sub-committee on instrument tubing supports (chairman, J. Johnston, Jr., also du Pont) are working on Recommended Practices 8 and 9.

Organize Additional Groups

Three new groups were organized at this 1948 Conference, according to Chairman Kerley. The sub-committee on the application of instrumentation to fractionating columns (chairman, D. M. Boyd, Jr., Universal Oil Products Co.) is to develop R. P. 10. It is believed that because fractionators can be classified generally by duty; i.e., de-butanizers, de-ethanizers, stabilizers, etc., this classification might be used as a criterion for instrumentation.

Safety is the topic of R. P. 11, the project of the sub-committee on handling of mercury (chairman, A. V. Novak, who recently joined Stanolind Gas & Oil Co. in connection with instrumentation in synthetic hydrocarbon research and development). This committeee's aim is to find some positive information in place of existing negative information on the storage, handling, and shipment of mercury, and the cleaning and servicing of instruments employing mercury. It is believed that data incorporating "do's" instead of "don't's" would be of greater help.

The last group, the sub-committee on procedures for instruments incorporating electrical equipment and used in hazardous environments (chairman, Porter Hart, Dow Chemical Co., Shreveport) is working on R. P. 12, also an attempt to compile a list of "do's" in place of "don't's."

Also Studying Education

Another group which has been concerned with a subject essential to better instrumentation is the Education Committee, with sub-committees on industrial instruments, electrical instruments, inspection and gaging, and optical instruments.

There has been no meeting of the entire Education Committee as yet; however, two sub-committees, those on industrial instruments and on inspection and gaging, have held organization meetings. The first has formulated a number of principles and aims. It has affirmed the need for a standard text for an industrial instrument education program on the mechanic level within industry. A recommendation has been made that the ISA sponsor the preparation of such a book.

150 Manufacturers Exhibit

A total of about 150 manufacturers of instruments and accessory equipment presented displays at Convention Hall. The value of the products exhibited was estimated at close to $10 million. No figures were released pertaining to the amount of business done either in actual or in potential sales, but it was reported that the petroleum industry users constituted a major portion of the active inquiries.

The technical meetings during the Conference were sponsored by the ISA, meeting jointly with the American Institute of Physics, the Industrial Instruments & Regulators Division of the American Society of Mechanical Engineers, and the Joint Sub-committee on Electronic Instruments of the American Institute of Electrical Engineers.

Effect of Fluid Pressure on Capacity Of Vertical Storage Tanks

By W. E. SPLAIN, M. E.
Socony Vacuum Oil Co., Inc.

THE PROBLEM of keeping an accurate inventory in large storage tanks has long been a troublesome one in the oil industry. During the summer there is a tendency for the inventory to gain, and during the winter for it to lose, in spite of the accuracy with which gage readings are taken.

This erratic behavior of large tanks is widely recognized by storage men, and for the most part has been ascribed to the effects of temperature on the material in storage.

A recent study of this subject was made, however, to determine the effect of other factors on tank inventory—factors which are usually ignored in tank calibration and gaging because they are considered negligible. These included:

1. The change in capacity of a tank due to stretching from the pressure of the liquid in the tank.
2. The change in capacity of a tank due to thermal expansion and contraction of the tank itself.

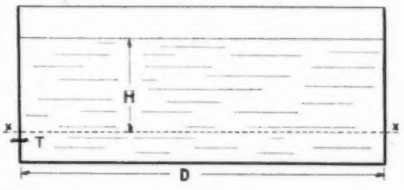
It was determined in the study that the first factor, fluid pressure, may increase the capacity of a 60,000-bbl. vertical tank by over 1600 gals. It was also determined that the same tank, if calibrated at 68° F., will hold over 1000 gals. more at 98° F. than at 68° F. Although these variations in capacity are minutely small on a percentage basis—less than 0.07 of 1% in the case of the effect of fluid pressure—on a gallonage basis they can accumulatively represent huge discrepancies over a period of time.

In the discussion which follows, the effect of the first factor, fluid pressure, is considered, and mathematical relations are developed to measure the capacity increase. The second factor, thermal expansion and contraction of the tank, will be covered in a following article. Only vertical tanks are considered.

Effect of Fluid Pressure

Suppose a vertical storage tank is empty when the peripheral measurements of the various rings are made for calibration purposes, that corrections are made for temperature, and that an accurate calibration chart is prepared showing the contents of the tank for each inch of liquid. When the tank is filled with liquid the shell is in tension and it stretches because steel is elastic. Obviously, therefore, the tank when full will hold more liquid than the chart would indicate. To determine how much more a tank will hold, the following mathematical analysis was made:

x-x = any plane under consideration (see sketch below),
I = increase in tank capacity in gallons in a ring 1 in. high due to elongation of the plate at the plane under consideration,
D = diameter of tank in feet,
H = height of the liquid column at plane x-x in feet,
W = weight of liquid in tank in lbs. per cu. ft.,
T = thickness of the plate at plane x-x in inches,
E = modulus of elasticity of steel, 29,500,000,
f_s = stress in plate at plane x-x in lbs. per sq. in.,
e = elongation of the tank plate at plane x-x, expressed as a fraction of the length of the plate,
C_i = increase in tank circumference due to elongation of the plate at plane x-x in feet,
R_i = increase in tank radius due to elongation of the plate at plane x-x in inches.



Then:

WH = fluid pressure at plane x-x in lbs. per sq. ft.; $WH/12$ = fluid pressure at plane x-x in lbs. on a strip 1 in. high and 1 ft. wide; and $WHD/12$ = fluid pressure at plane x-x in lbs. on a strip 1 in. high and D ft. wide. This latter value equals the force tending to rupture the plate.

The force exerted by the plate itself in a ring 1 in. high at plane x-x, in lbs., $= 2Tf_s$. Therefore:

$$2Tf_s = WHD/12$$

and

$$f_s = WHD/24T$$

This relation determines the stress in the steel due to fluid pressure at any plane x-x.

According to Hooke's Law, the stress in a piece of steel in lbs. per sq. in. divided by the elongation of the piece equals the modulus of elasticity of steel. From which:

$$f_s/e = E = 29{,}500{,}000$$

and

$$e = f_s/29{,}500{,}000$$

where e = a fraction that defines the proportional increase in tank circumference.

Since πD = circumference of the tank in feet, then

$$\pi De = C_i$$

where C_i is the increase in tank circumference in feet due to elongation of the plates at plane x-x.

Substituting for e in this equation:

$$\frac{\pi D f_s}{29{,}500{,}000} = C_i$$

and

$$\frac{12\pi D f_s}{2\pi \times 29{,}500{,}000} = R_i$$

where R_i is the increase in tank circumference in inches due to elongation of the plates at plane x-x.

Where the ratio of the increase in tank radius to the tank diameter is very small, I, the increase in tank capacity in a ring 1 in. high, can be very closely approximated by multiplying the increase in tank radius (in inches) by the circumference of the tank (in inches). This value will be in cubic inches, which can be converted to gallons by dividing by 231, so that:

$$I = \frac{R_i \times 12\pi D}{231}$$

By substituting for R_i:

$$I = \frac{12\pi D f_s}{2\pi \times 29{,}500{,}000} \times \frac{12\pi D}{231}$$

$$= \frac{72\pi D^2 f_s}{29{,}500{,}000 \times 231}$$

By substituting for f_s:

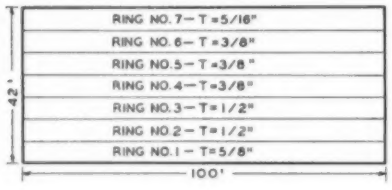
$$I = \frac{72\pi D^2}{29{,}500{,}000 \times 231} \times \frac{WHD}{24T}$$

$$= \frac{WHD^3}{723{,}000{,}000\,T}$$

The final formula derived above is a general formula for the increase

in gallons in any inch of height. It will be observed that I varies as the cube of the tank diameter; therefore, the values of I will increase rapidly as the diameter of the tank increases.

Suppose we consider the application of this formula to a tank such as shown in the sketch below, having a diameter of 100 ft, a height of 42 ft. made up of 7 equal rings with thicknesses as shown, and containing No. 1 Fuel Oil (W = 51.2 lbs./cu. ft.).



From the formula previously derived:

$$I = \frac{51.2 \times 1{,}000{,}000 \times H}{723{,}000{,}000 \times T} = .071 \frac{H}{T}$$

Since the thickness T of the plates varies from one ring to another, it is necessary to determine the increase for each ring (or for each group of rings of the same thickness) separately.

Therefore, considering the bottom ring (no. 1) first, when the tank is full the head on the bottom inch of this ring is 42 ft. Since the plate is ⅝-in. thick, for the bottom inch of ring no. 1:

$$I = .071 \times \frac{42}{0.625} = 4.76 \text{ gals.}$$

The head on the top inch of the same bottom ring is only 36 ft., so that for the top inch of ring no. 1:

$$I = .071 \times \frac{36}{0.625} = 4.08 \text{ gals.}$$

It will be noted from the equation that I varies directly as the head H. Therefore, the average value of I for each inch of the bottom ring is:

$(4.76 + 4.08)/2 = 4.42$ gals.

Since the ring is 72 in. high, the increase in capacity for the entire bottom ring is

$72 \times 4.42 = 318$ gals.

Similarly, the increase in capacity can be computed for the remaining six rings, to arrive at the total increase in capacity for the entire tank. The calculations can be tabulated in some such form as shown in Table 1.

TABLE 1—Tabulation of Calculations

Ring No.	T, Inches	H at Bottom of Ring, feet	H at Top of Ring, feet	I for Bottom Inch, gals.	I for Top Inch, gals.	Average I for Entire Ring, gals.	Increase in Capacity of Ring, gals.
7	5/16	6	0	1.36	0	0.68	49
6	3/8	..	6	...	1.14	2.84	614
5	3/8	..	..	...	...		
4	3/8	24	..	4.54	...		
3	1/2	..	24	...	3.41	4.27	615
2	1/2	36	..	5.12	...		
1	5/8	42	36	4.76	4.08	4.42	318
	TOTAL INCREASE IN TANK CAPACITY, GALS.						1596

An alignment chart, Fig. 1, has been prepared for the graphic solution of the equation. Although it gives only an approximate answer, like any graphic means of solution of an equation, it can be used to make these calculations with reasonable accuracy.

Conclusions

The following conclusions are suggested by the above analysis:

1—Where accurate gaging of large diameter tankage is required, the effect of fluid pressure on the size of the tank may become an appreciable factor.

2—The effect is more pronounced in large diameter tanks since the change in capacity varies as the cube of the tank diameter.

3—A tank will hold more volume of heavy liquid than of light liquid.

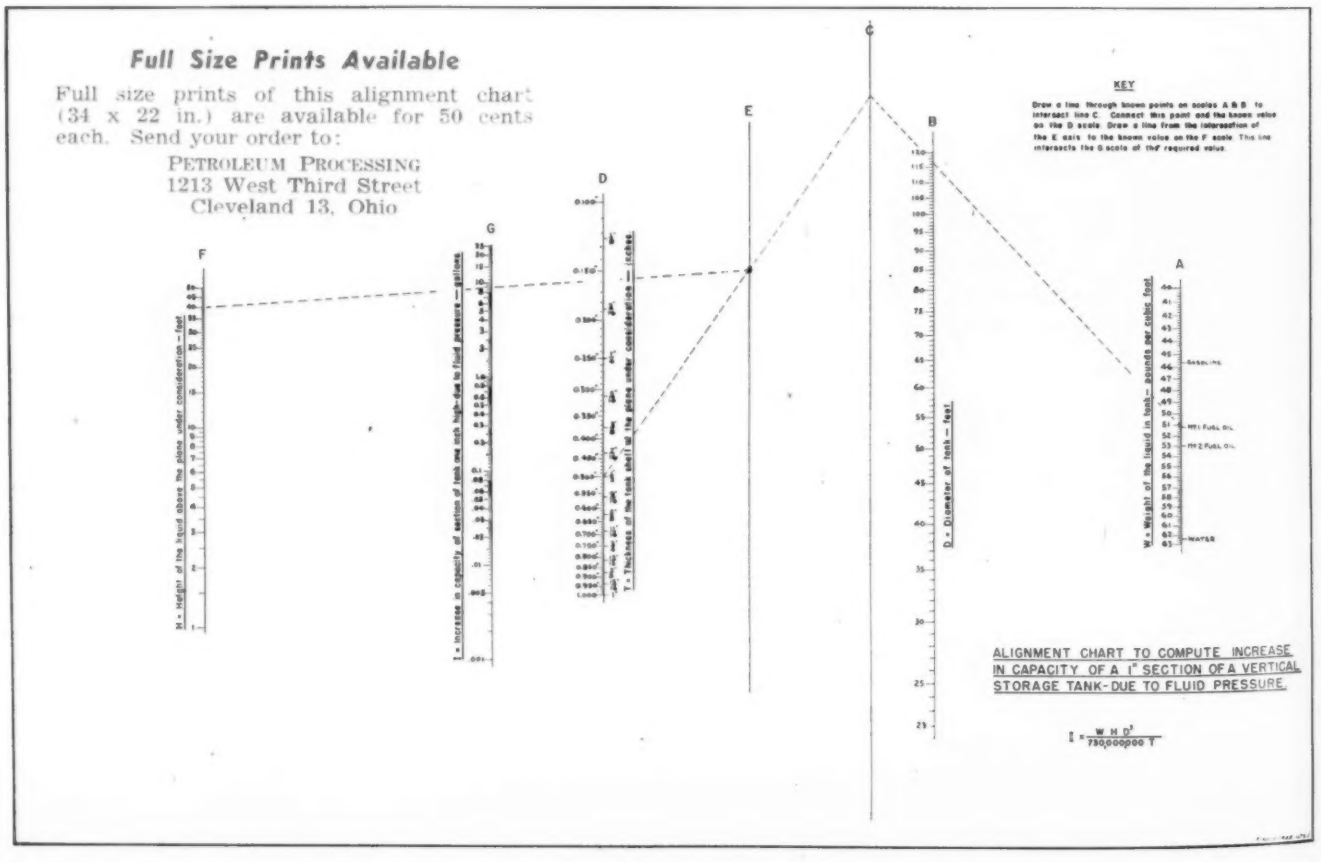
4—If a tank is calibrated when full of liquid, the error in inventory will be less than if calibrated empty.

5—When tanks are calibrated, the effect of fluid pressure can readily be taken into consideration.

Full Size Prints Available

Full size prints of this alignment chart (34 x 22 in.) are available for 50 cents each. Send your order to:

PETROLEUM PROCESSING
1213 West Third Street
Cleveland 13, Ohio


KEY
ALIGNMENT CHART TO COMPUTE INCREASE IN CAPACITY OF A 1" SECTION OF A VERTICAL STORAGE TANK - DUE TO FLUID PRESSURE.
$I = \frac{W \cdot H \cdot D^2}{730{,}000{,}000 \cdot T}$

World's Largest Solvent Lube Units Installed in Cit-Con Refinery

IMPROVEMENTS of the past several years in the technology of lubricating oil and wax manufacture are embodied in the processes and equipment being installed in the refinery of the Cit-Con Oil Corp., at Lake Charles, La. Designed and engineered from the ground up about a year ago, the plant is scheduled to be in operation in 1949.

The refinery, which will be the largest in the U. S. designed exclusively for the production of solvent refined oils and wax products, is owned jointly by Cities Service Co. and Continental Oil Co. It will charge selected reduced crude from Louisiana, Arkansas and East Texas, supplied from the present light oil refineries of Cities Service and Continental Oil Co. at Lake Charles.

Normally finished oil blending stocks will be delivered from the Cit-Con plant to the parent companies to be blended in their respective installations. A small bulk blending tank installation is being provided for tank car shipments. In addition, barge and tanker loading facilities are being provided. Gas oil, solvent extracts and various wax by-products will be returned to the Cities Service and Continental refineries for cracking or fuel oil use.

The Cit-Con refinery is designed to produce 6000 B/D of 95 Viscosity Index lubricating oil and will also have provisions for producing oils of 100 VI. Additional specially designed equipment will provide for the manufacture of fully refined crystalline wax to meet requirements for such uses as coating for milk containers, food packages and other paper products.

The charging stock for the plant will be a mixed reduced crude in the order of 30-35% on crude, amounting to 25,000 B/SD. The stock will be charged to two identical vacuum distillation units, each with a processing capacity of 12,500 B/D and supplying the products shown in Table 1.

The distillate cuts from the vacuum towers will be solvent refined in the largest single furfural unit ever to be constructed. It will be capable of circulating 30,000 bbls. of solvent daily and will have a processing capacity of 6400 to 11,000 B/D, depending on the stock charged.

The bottoms from the vacuum distillation towers will be charged to a Duo-Sol unit to produce bright stock. In this process a blend of phenol and cresylic acid along with

TABLE 1—Typical Yields from Vacuum Distillation Unit at Cit-Con Lubricating Oil Refinery

Cut	% on Crude	B/SD	Gravity, ° API
Gas Oil	3.8	1,430	30.2
100 Neut.	5.8	2,180	27.9
200 Pale	6.0	2,260	26.4
Lt. Int.	2.2	830	24.8
Hvy. Int.	4.4	1,660	23.7
Bottoms	11.0	4,140	15.6
TOTAL	33.2	12,500	

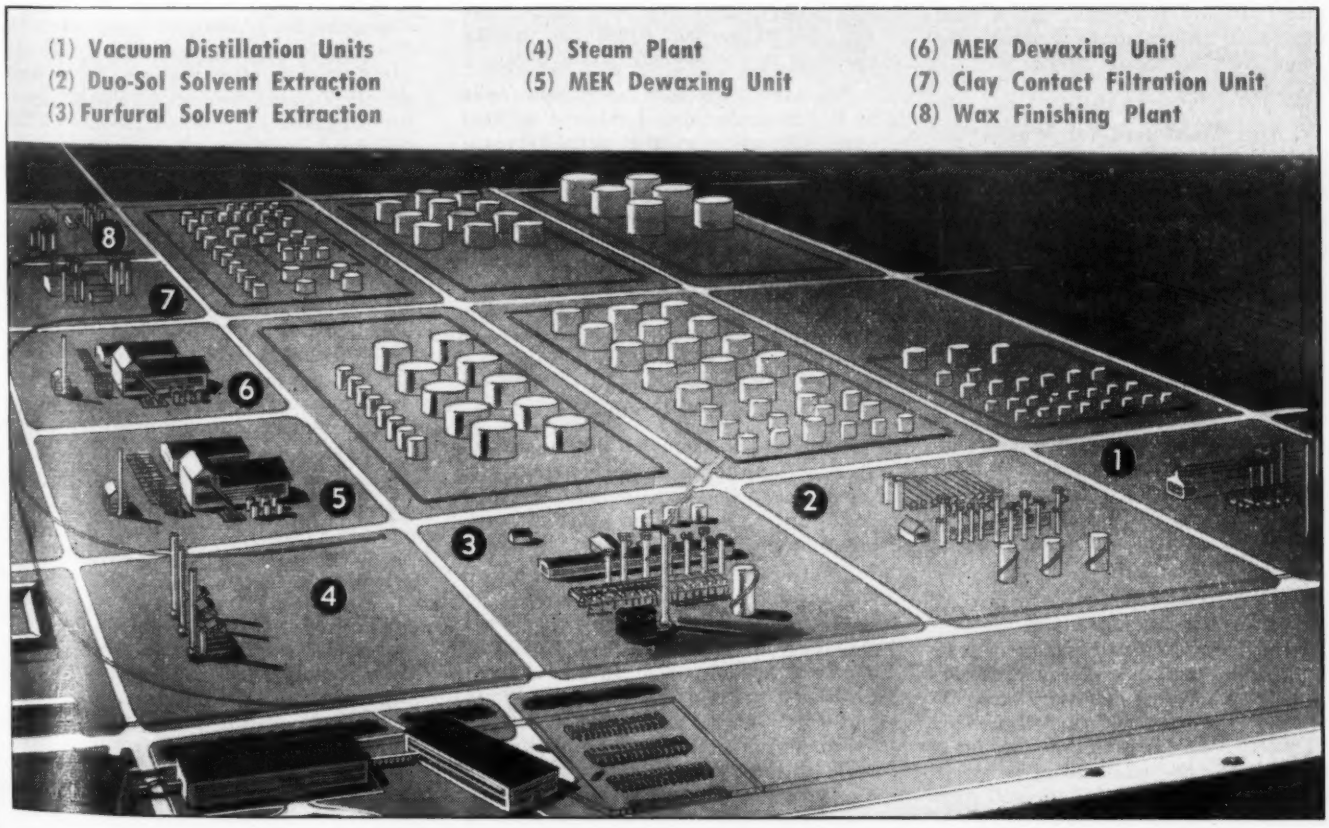


Fig. 1—General arrangement of processing units in new Cit-Con plant

propane is used to remove undesirable compounds from the oil. The Duo-Sol unit will have a raw oil processing capacity of 9700 B/D and will be the largest of its type ever to be constructed.

Dewaxing of all solvent refined raffinate stocks will be done in two MEK solvent dewaxing units, which utilize a blend of methyl-ethylketone, benzene and toluol in the separation of the wax from the oil. One MEK unit will dewax the three lightest distillate stocks, processing approximately 4800 B/D of charge oil for the production of zero pour oils. This unit will come into operation as a normal sequence plant, producing low oil content, high tensile strength specification waxes. This plant is so arranged, however, that it can be converted to a reverse sequence plant if desired. The second dewaxing unit is designed to handle the heavy intermediate distillate and the bright stock and includes a repulping step after the primary filtration. The second MEK unit will process around 4300 B/D of charge oil.

Clay finishing of oils at the Cit-Con plant will be carried out in two duplicate contact filtration units, one will process oils from the first dewaxing plant, handling up to 3700 B/D of charge. The second clay contacting unit will handle up to 3200 B/D of charge from the second dewaxing plant. Providing the clay contacting units with sufficient capacity to handle the production at the rate coming from the dewaxing units, will allow keeping at a minimum the intermediate tankage between the dewaxing plant and the clay contacting unit.

Acid Treatment for Waxes

The final step in refining the crystalline waxes to remove odor and taste and improve color will be accomplished through acid treatment, followed by percolation through bauxite clay using standard percolation filter equipment.

In addition to the process units the Cit-Con lubricating oil plant will be furnished with complete auxiliary services such as utility distribution system, refinery waste disposal system, tank farm and transfer system, tank car and barge loading facilities, warehouses and mechanical shops. The administration buildings consist of three buildings, an office, laboratory and change house.

Power will be furnished to the Cit-Con refinery from the adjacent Cities Service Refining Corp. generating station. The plant will have its own boiler house which will consist of three 125,000 lbs./hr. boilers with provision for the addition of a fourth unit at a later date. Boilers will generate 600 lbs. steam which, except for a few high pressure turbine drives, will be used to drive the propane refrigeration compressors in the twin MEK solvent dewaxing units.

F. M. Simpson, vice president and general manager of Cit-Con since its organization

There are three sets of compressors, two of which will exhaust at 200 lbs. back pressure while the third will be operated condensing. In normal operation one back pressure compressor and the condensing compressor will be operated, with the other 200 lbs. back pressure compressor being used in place of the condensing unit, as other drives elsewhere in the refinery are switched from electric to steam in order to satisfy changes in the overall steam balance.

The extensive use of steam coils in the tank farm will cause a significant difference in the overall steam balance between winter and summer operations. In addition to the 600 lbs. steam system, there will also be 200 lbs. steam and exhaust steam both clean and dirty. Other utilities to be distributed throughout the plant are cooling water, well water, plant and instrument air, gas, fuel oil and fire protection water.

Three Wells Supply Water

Three wells located in the plant area will provide make-up water for the refinery and for operation of the 51,000-gpm circulating water cooling tower. Natural gas will be used for all furnaces and boilers.

The tank farm will consist of some 135 storage tanks having a total capacity of approximately 2,000,000 bbls. Many of these tanks will be furnished with steam heating coils and a number of tanks are also to be provided with electric motor driven tank agitators for the prevention of stratification and uniformity of oil being withdrawn. An interesting feature of the finished oil storage tanks is the provision to these tanks of a constantly circulating atmosphere of dehumidified air to prevent atmospheric condensation in the empty portions of such tanks during climatic changes. Heretofore steam coils have often been located under the roofs of such tanks for this purpose but this is the first installation as far as is known in which air conditioning type Alumina dryers have been installed. The indications are that this method is less costly than the use of steam coils and it was selected not only for this reason but also because of the critical situation in pipe.

The Cit-Con plant is located on a 367-acre tract near the Cities Service refinery at Lake Charles and approximately 10 miles from the Continental Oil Co. refinery. The refinery is laid out in an L-shape with the tankage situated inside the L for maximum operating efficiency. A laboratory being built adjacent to the administration buildings will contain equipment for daily control and analytical work, crude oil evaluations, process unit studies and research on wax. Fig. 1 shows the general arrangement of the processing units, tankage and buildings at the Cit-Con refinery.

Company Formed Last Year

The Cit-Con Oil Corp. is 65% owned by Cities Service and 35% by Continental Oil Co., with executives of the two companies making up the board of directors and was formed in the summer of 1947 to build and operate the new lubricating oil refinery. F. M. Simpson has been vice president and general manager of Cit-Con since its organization. He was previously for several years superintendent of refineries for Cities Service Oil Co. (Del.) and had been in this company's service since 1923.

W. Alton Jones, president of Cities Service Co., is chairman of the board of Cit-Con, and Burl S. Watson, vice president of Cities Service, is president. Harold Osborn, vice president of Continental and A. P. Frame, vice president of Petroleum Advisers (Cities Service subsidiary) are vice presidents of Cit-Con.

Remaining directors are H. L. O'Brien, L. D. Mann and G. L. Mateer of Cities Service and E. F. Battson, Serge B. Jurenev and J. W. Liddell of Continental Oil Co.

The Lummus Engineering Co., New York, designed and is constructing the Cit-Con refinery, with the exception of the Duo-Sol unit which is being built by the Max B. Miller Co., New York. The architectural firm of Walker and Poor Co. designed the laboratory, the locker and cafeteria building and the administrative building.

Organic Chlorides in Wyoming Crudes Found Cause of Plant Corrosion

A STAFF REPORT by the Editors of Petroleum Processing

LANSING, Mich. — Corrosion problems in the refining of sour crude oils from Wyoming and West Texas fields, particularly those from Wyoming, represented a subject of high interest at the Regional Technical Meeting of the Western Petroleum Refiners' Assn. here Aug. 27.

In addition to a high sulfur content, the Wyoming petroleum has an organic chloride content almost ten times that of other sour and sweet crudes. As a result, it was reported to be a troublemaker by causing hydrochloric acid corrosion in addition to the conventional and expected sulfur corrosion according to one Illinois refiner.

This and other problems were brought out in a paper, "Processing Sour Crudes at Globe, Lemont Refinery," presented by Ralph B. Pierce, superintendent, Globe Oil & Refining Co., Lemont, Ill. WPRA members and guests participated in a lengthy discussion period following the paper, and fired questions at Mr. Pierce and his co-authors, Dr. William G. Krause, chief chemist, and Jack M. Lawson, chief engineer, for Globe.

Wyoming Shipments Growing

It should be pointed out that the quantity of crude oil moving out of Wyoming is not particularly significant in comparison to total U. S. refining figures, being some 68,000 b/d (June, 1948, average). However, the volume has increased over last year, as indicated in Table 1. The proportion of sour crudes to sweet produced throughout the country has not changed markedly since 1925, according to recent Bureau of Mines reports.[1] However, total crude production in that same period has almost doubled. As a result, the larger production of the sour crudes has had to be sent to more widely distributed refineries. This has meant increased operating and maintenance problems for many plants who for years have charged nothing but sweet stocks to their units.

Globe Oil & Refining Co. for the past several years, in a plant of 27,000 b/d charge capacity, has been operating on between 25 and 50% sour crudes. The West Texas stock, with a sulfur content of about 2%, is brought in by pipeline from the Slaughter field. The Wyoming crudes come in by tank car and pipe line from Elk Basin (1.72% sulfur) Byron Basin (2.42% sulfur), and Oregon Basin (3.27% sulfur).

The high percentage of organic chlorides in the Wyoming stock was found to cause severe corrosion through the formation of hydrochloric acid in Globe's Perco bauxite catalytic desulfurization unit, Mr. Pierce said.

"After this unit had been operating a short time," he explained, "a leak developed in the overhead condenser off the secondary fractionating tower, and on examination it was found that severe corrosion had taken place. Analysis of the corrosion products and the water condensate showed the corrosion was caused by hydrochloric acid. This was a definite surprise because no past experience or other information indicated any possibility of this type of corrosion. Ammonia was injected as means of immediately neutralizing the acid and an investigation was started to determine the cause and source of the material."

It was decided that the acid must come from the feed to the unit or be present in the catalyst itself. The catalyst was examined and found to contain no hydrochloric acid or chloride of any kind. Preliminary examination of the gasoline feed to the unit showed no trace of entrained water or acid. Combustion analysis of the gasoline feed stock showed the presence of chlorinated hydrocarbons, and this gave the clue to the cause of the hydrochloric acid corrosion. These chloroparaffins cracked when passed through the bauxite catalyst at operating temperatures (700-800° F.) with the formation of hydrochloric acid and probably an olefinic hydrocarbon. The acid then attacked the metal in the condenser at the point of condensation.

"Since we were processing several types of crude it was felt we should find out which crude was responsible for this condition," Mr. Pierce said. "Five grades of crude, West Texas, Wyoming, Illinois, Kansas and Louisiana, were studied in a laboratory investigation. Each crude was carefully fractionated and 2% fractions taken off to a top vapor temperature of 400° F. These samples of gasoline were then analyzed for organic chloride after a caustic wash to remove any entrained hydrochloric acid.

Ten Times as much Chlorides

"It was found that Illinois, Kansas, Louisiana, and West Texas crudes contained little or no organic chlorides in the gasoline fractions. However, the Wyoming crude contained approximately ten times as much as the others and most of this was found to be concentrated in the gasoline range between 250 and 350° F. Consequently it was decided that Wyoming crude was responsible for the corrosion problem on the unit. This was further substantiated when this type crude was discontinued for several months and the evolution of acid became almost negligible. However, the ammonia effectively neutralized it so no further difficulty was experienced."

A comparison of organic chloride contents of some of the crudes, as obtained by Globe chemists, is shown in Table 2. In explaining the method of analysis, Globe's chief chemist, Dr. Krause, said, "Each crude was fractionated in an all-glass still packed with glass Fenske rings. The caustic wash was made because the crude samples were not desalted and there was some hydrolysis of the calcium chloride in the salt with subsequent formation of hydrochloric acid. In plant operations the crude is desalted and little or no calcium chloride is left in it. The washed

TABLE 1—Shipments of Crude Oil from Wyoming

(42-gal. U. S. bbls. daily average)

To:	June, 1948*	1947**
Colorado	8,200	11,200
Illinois, Minnesota, Wisconsin	16,300	11,600
Indiana	10,250	8,700
Kansas, Nebraska	10,200	2,700
Michigan	4,400	1,600
Montana, Idaho	17,400	16,800
Utah	970	1,280
TOTALS	67,720	53,880

* Source: Ohio Oil Co., Statistical Department.
** Source: American Petroleum Institute.

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TABLE 2—Organic Chlorides Analyses of Two Sour Crude Gasoline Cuts

WEST TEXAS		WYOMING	
Tower Temp. in °F.	% Chlorides as Cl	Tower Temp. in °F.	% Chlorides as Cl
144	.....	108	.....
158	0.0005	140	.....
183	0.0005	172	0.0006
210	0.0006	181	0.0013
216	0.0007	194	0.0055
223	0.0009	255	0.0070
239	0.0009	271	0.0162
250	0.0008	286	0.0187
273	0.0007	302	0.0175
289	0.0006	320	0.0056
307	0.0007	340	0.0031
327	0.0005	358	0.0015
342	0.0005	379	0.0016
363	0.0010	385	0.0016
381	0.0018	400	0.0012

samples were analyzed for organic chloride by combustion and absorption of combustion products in standard alkali solution. Chloride was determined by precipitation as silver chloride and comparison in Nessler tubes. Blanks were run on the entire operation to establish purity of reagents."

In the analysis of the Wyoming crudes, 1% cuts were taken off, he said. With the other four samples, 2% cuts were used. In all cases, determinations began with an 1800 ml. sample.

Other Refiners Questioned

Questioned since the WPRA meeting by PETROLEUM PROCESSING, only one of a representative group of Wyoming refiners reported corrosion of this type. Frontier Refining Co., at Cheyenne, does not operate a desulfurization unit, but has experienced similar corrosion in the topping units, according to Harry A. Brown, superintendent. Ammonia injection has retarded but not stopped this corrosion, he stated. Frontier's refinery has a crude charge capacity of 8800 b/d, and the company operates a 4950 b/d cracking unit.

The corrosion occurs in the upper five feet of the fractionator and in the overhead condensers on the topping unit, with some corrosion also in the receiver, according to Mr. Brown. Metals involved are both carbon steel and admiralty alloy. The tower top temperature is about 270° F. In the overhead condenser it ranges from 270 down to 100° F. Frontier uses an average of 0.002 lbs. ammonia per bbl. crude oil throughput in the unit. It is injected as a gas from its own pressure in cylinders into the top of the crude unit column. The amount used is determined by the pH of the receiver water. This value is kept to about pH 7.6, Mr. Brown stated.

Another Wyoming refiner stated his plant had experienced only mild corrosion in gasoline fractionating equipment, and thus far has obtained satisfactory control with alloys. However, he believes the corrosion is caused by hydrogen sulfide and has not investigated for organic chlorides.

Another unusual form of corrosion experienced by Globe and discussed at the Lansing meeting is that of the so-called "Hydrogen blisters". Coming to light only recently, the phenomenon observed at the Lemont refinery checks with information reported recently by two other companies.

This corrosion manifests itself in the form of blisters on the outside walls of tanks and vessels. Casual observation leads the inspector to take them for paint blisters, Mr. Pierce stated. However, they are actually blisters in the metal itself, caused by a bubble of gaseous hydrogen within the metal and close to the outer surface. Tests have shown the gas to be under very high pressures, as much as 2,700 psi. Occasionally it ruptures the thin outer wall of the blister with the resulting weakening of the structure. The blisters vary in size all the way from tiny lumps the size of a penny to huge, irregular shapes of up to 2 to 3 sq. ft. in area.

Metal Reacts with H_2S

The theory as to their cause is that hydrogen sulfide in the fluid within the tank reacts with the metal to produce hydrogen, which in turn diffuses outwardly, with the formation of bubbles, or "blisters."

Globe's experience with this type of corrosion checks with that reported by two other companies in papers presented last April at the annual meeting of the National Assn. of Corrosion Engineers in St. Louis.

Tests on the blisters on Phillips Petroleum Co. tanks, on one vessel showed the load-carrying capacity of the metal to be reduced by about 20%, according to M. H. Bartz and C. E. Rawlins of Phillips in their NACE paper, "Effects of Hydrogen Generated by Corrosion of Steel." In another paper at that same meeting, Nathan Schofer of Cities Service Refining Corp., Lake Charles, La., reported observing the same hydrogen penetration and blister formation in several process vessels.

Other types of corrosion and methods for prevention as told by Mr. Pierce were of the conventional type. The practice is to keep sour and sweet crudes segregated in the Lemont refinery storage tanks, he said, with the West Texas and Wyoming crudes mingled in floating roof tanks, and the other sweet crudes kept in fixed roof tanks.

In operating, the 9000 b/d topping unit is run on 100% sour crude all of the time, except for a 24-hr. period before a scheduled shutdown for inspection. It has been found from experience that dangers from hydrogen sulfide are much less when the unit is shut down with sweet crude in the system. The company's 22,000 b/d combination unit is operated intermittently on both kinds of stock; the only sour crude processed in it is the amount in excess of the capacity of the topping unit.

High Sulfur Asphalt Is Brittle

Vacuum reduced residuum at Lemont is used for flux oil for roofing asphalt, and as such is sold to another company engaged in that field. In general, the high-sulfur flux oil is not as satisfactory as that from sweet crude, Mr. Pierce explained, because on oxidation the high sulfur flux oil blows down to a very hard and brittle asphalt with low weathering value. Globe's buyer of this material has, however, solved the problem by using a commercial additive material which produces a highly satisfactory roofing asphalt. The additive is usually the hydride of ferric chloride, according to Mr. Pierce, although zinc chloride can also be used. It is not merely mixed with the flux oil before blowing, but must be fed into the blowing still during processing.

The residual fuel oil market is somewhat restricted by sour crude operation at Lemont. "However, the intermittent operation is advantageous because low and high sulfur fuels can be segregated," Mr. Pierce stated. "The low-sulfur fuels are used for industries requiring them, such as open hearth steel furnaces, malt driers, etc. High-sulfur fuels are entirely satisfactory for heating purposes, steam generation, and the like. The cracked asphalts from high sulfur crude are entirely satisfactory for road oils."

Globe uses a Girbotol amine unit to remove hydrogen sulfide and then a caustic washer to remove mercaptans from the C_3-C_4 feed for the polymerization unit. In 15 months operation, they have run over 1,000,000 bbls. of poly feed on the original charge of amine in the Girbotol unit with no loss of chemical or decline in its activity.

References

(1) "Sour Crudes-Trends in Supply," by H. M. Smith and O. C. Blade, U. S. Bureau of Mines, Bartlesville, Okla.; presented at Annual Meeting, American Petroleum Institute, Chicago, Nov. 10-13, 1947.

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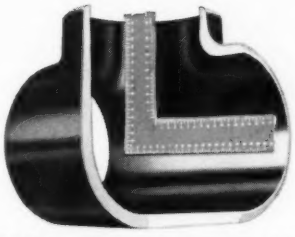

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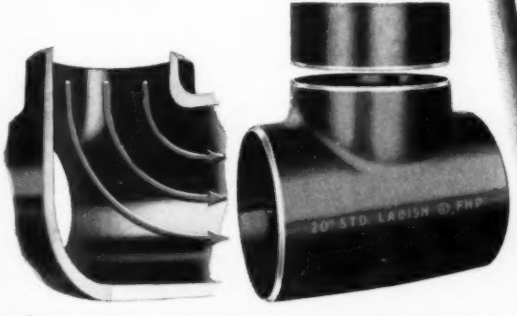

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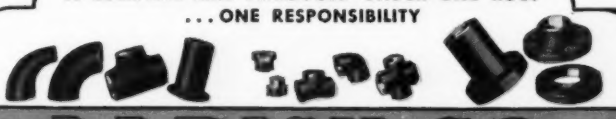

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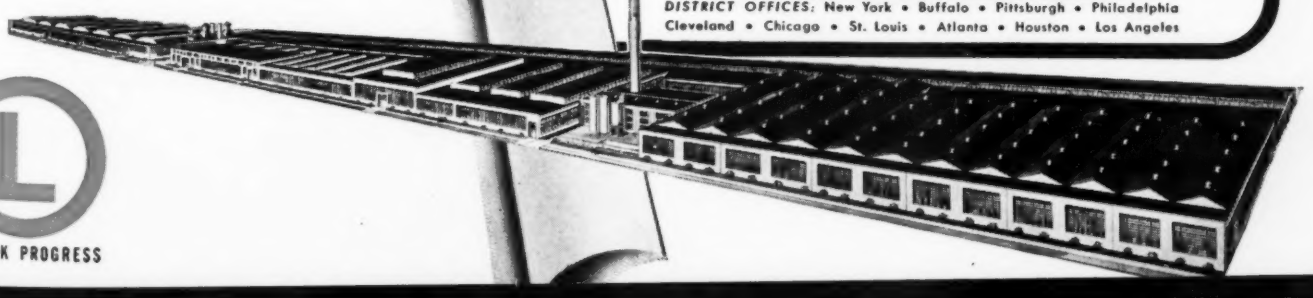

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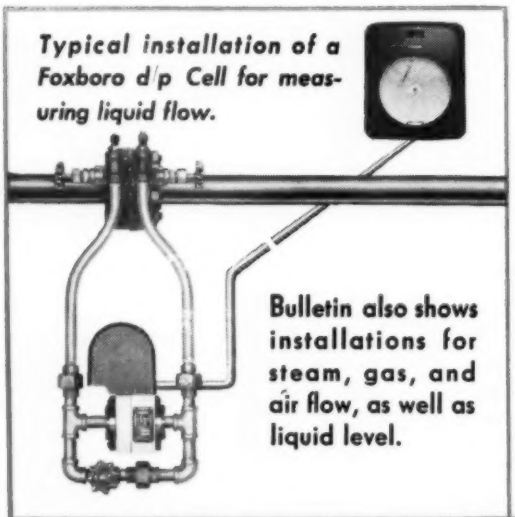

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Design of System for Controlling Combustion in Refinery Heaters

On this and the following pages are presented reviews and abstracts of selected papers presented at the recent Conference of the Instrument Society of America in Philadelphia, Sept. 13-17, 1948.

(Review of paper entitled "Experimental Application of Combustion Controls to a Process Heater," by W. E. Boyle, Shell Oil Co., and P. R. Hoyt, Shell Development Co., presented at National Instrument Society Conference, Philadelphia, Sept. 13-17, 1948.)

A PROGRAM for fuel conservation at the Wood River, Ill., refinery of Shell Oil Co., Inc., called for efficient combustion control in heaters. Although it was impractical to design a suitable system applicable to refinery process heaters in general, it was felt that basic principles of combustion control methods could be applied to many heaters.

To establish these principles from a practical viewpoint an experimental installation was made. A heater was selected where the only operating requirement was to release heat in an amount and at a rate to elevate and maintain the temperature of the flowing oil at a constant predetermined value.

The heater was a conventional radiant type, two-cell, natural draft furnace fired by 14 burners from each side wall, designed for 50,700,000 BTU per hour heat release. The burners are of the conventional combination fuel gas, fuel oil-atomizing steam type. Oil enters in two parallel streams from a common header, flows through the convection tubes, roof tubes, floor tubes and then out to a common header.

To obtain combustion control it is necessary to measure and indicate or record the instantaneous flow rate of fuel and combustion air, and then to regulate these two variables. Measuring fuel flow offered no problem as there already were meters on both the fuel oil and fuel gas lines. Means for actual measurement of air flow, however, were not immediately apparent. The conventional methods used with forced air systems obviously could not be applied on natural draft furnaces of this type.

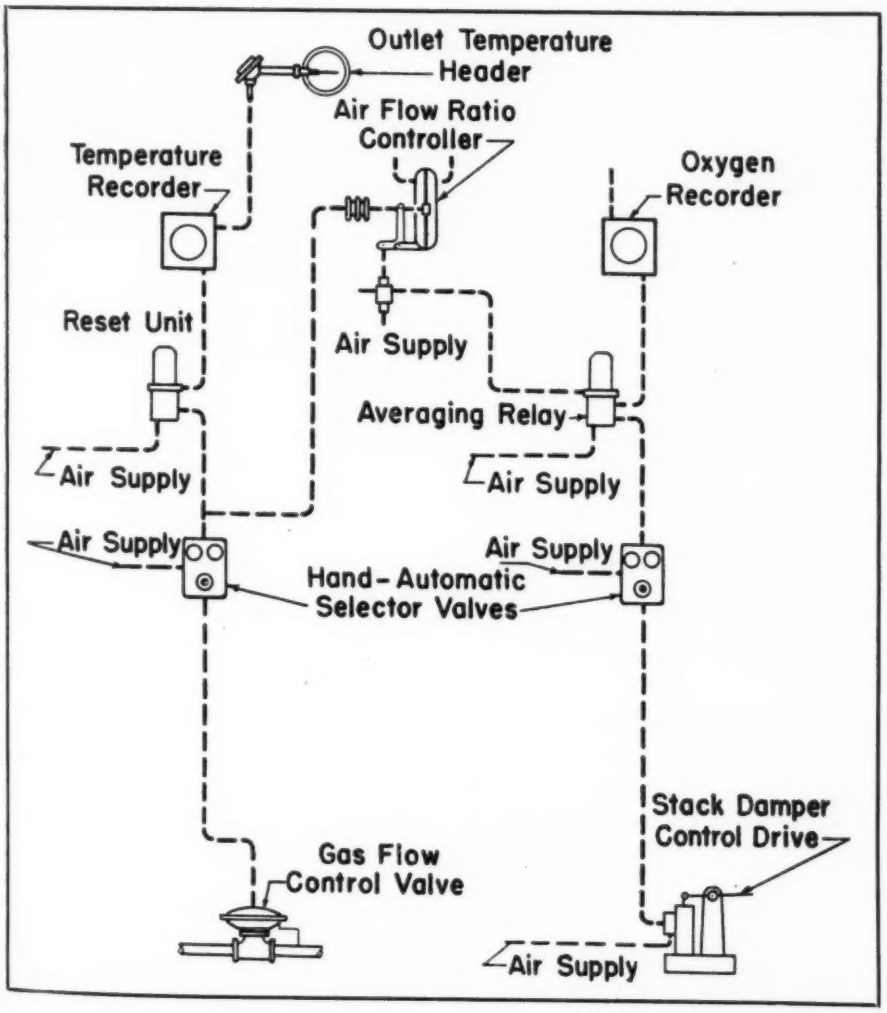
It was decided, therefore, to use the fire box pressure as an indication of the rate of air flow. If the burner air ports are considered as a fixed orifice, then the differential pressure between fire box and atmospheric pressure is related to the rate of air flow through the ports.

For measuring this differential, two slack diaphragm type differential indicators were provided for each fire box. In order to insure measurement of actual differential pressure across the burner ports, the high pressure lead from the differential unit was located with its open end adjacent to and in the same plane as the admospheric side of the burner ports. The low pressure lead terminated in the firebox. These instruments not only provided a means for detecting air flow changes, but also served as a guide for equalizing both cells of the furnace.

To provide automatic control of air flow, it was a simple matter to connect the low pressure side of the measuring element of a differential pressure controller to the furnace and have the controller output pressure position the uptake draft damper. This was equivalent to a conventional differential type flow control system.

This instrumentation provided means for measuring and controlling the total combustion air flow for a fixed heat load only. But the fuel flow is automatically varied by means of a temperature controller in the oil outlet line, the output air pressure of which loads a pressure balanced type diaphragm valve in the fuel gas line.

To vary air flow simultaneously with fuel flow, the temperature controller output pressure, which is proportional to the heat load demand,



Drawing courtesy Bailey Meter Co.

Fig. 1—Schematic diagram of instrumentation for controlling combustion in a heater

was utilized and connected to the air flow controller through an adjustable ratio mechanism. For a given ratio adjustment, this pressure sets up a proportional demand for air flow which is satisfied only when balance is restored by the flow controller. Thus a method was provided for automatically changing the rate of air flow in a predetermined ratio with fuel flow changes demanded by the temperature controller.

One objectionable feature of the system developed thus far is that the ratio of fuel flow to air flow, which should be a fixed ratio regardless of heat load, cannot be maintained unless the ratio mechanism is manually readjusted as the load changes. To maintain automatically the desired ratio over the complete operating range it was decided to measure the oxygen content of the combustion gases as an indication of the amount of excess air. An oxygen analyzer and a recorder controller were therefore installed.

Flow Diagram on Previous Page

A schematic diagram of the complete control circuit with component parts is shown in Fig. 1. The control unit of the temperature recorder is of the conventional pneumatic type with adjustable proportional band. The output loading pressure is transmitted to a standardizing relay, providing proportional speed-floating action. The output pressure from this unit, representing fuel demand, loads the pressure balanced diaphragm control valve in the fuel gas line through a manual automatic selector valve. This same loading pressure is also transmitted to the ratio mechanism of the air flow controller where it is balanced against a differential pressure which represents the measurement of the rate of air flow. The resultant output pressure is connected to one chamber of an averaging relay or totalizer. The other chamber of this relay is loaded by the output pressure of the oxygen recorder controller. The relay output pressure, equal to the sum of these two pressures, is connected through a manual automatic selector valve to the power piston positioning the stack damper. The damper controls the rate of air flow. The control unit of the oxygen recorder has adjustable proportional band action.

To illustrate the sequence of operation, let us assume a state of equilibrium. Heat is being supplied in an amount and at a rate to hold the outlet temperature of the oil at the control point. Also, the rate of air flow is proportioned correctly with fuel flow to maintain the oxygen content of the flue gas at a value selected to give the most efficient combustion.

Furthermore, let us assume that due to a heat load increase the outlet temperature falls below the desired value. With a drop in temperature, the output loading pressure increases a proportionate amount, causing the pressure balanced valve to open until the fuel gas pressure increases to again balance the loading air pressure. (This loading pressure continues to increase, due to the reset action of the standardizing relay, until the temperature returns to the control point.) The higher gas pressure produces a higher differential across the burner orifices thus increasing the fuel gas flow rate.

At the same instant that the gas flow increases, the combustion air flow rate increases in a related amount depending on the ratio adjustment between the loading pressure and differential pressure representing air flow. If the increased fuel and air flow rates are not in the correct ratio to maintain the same combustion efficiency, the resulting change in per cent of oxygen in the flue gas will cause an offset from the control point of the oxygen controller. Output loading pressure changes proportionately, increasing with a decrease of oxygen and decreasing with an increase of oxygen. The output pressure from the averaging relay in turn changes an equal amount, repositioning the uptake damper and causing a rate of air flow change in a direction and an amount to return the oxygen content to the desired value.

Ratio Controller Not Necessary

In actual practice it was found that most of the corrective action for maintaining combustion efficiency is furnished by the oxygen controller. In view of this fact and the negligible time lag of the oxygen control circuit, the air flow ratio controller was later disconnected from the control system. The averaging relay was reconnected as a standardizing relay furnishing proportional speed-floating action for the oxygen controller. With this arrangement the temperature controller operates only the fuel gas valve, and the oxygen controller operates the stack damper independently.

The improvement in combustion efficiency attributable to the controls represents a reduction of fuel consumption averaging 15%. Based on fuel savings alone the payout time for the complete installation on this furnace was approximately 3½ months.

It has definitely been established by this experimental installation that further savings of fuel are not limited by lack of suitable measuring and controlling devices, but rather by the inadequacies of present burner and furnace design.

* * *

EDITOR'S NOTE: Copies of the complete text of the preceding paper (No. 48-3-2) are available. See box, pg. 948.

Use of the Multi-Element Control System in Refineries Illustrated

(Review of paper entitled "The ABC's Of Multi-Element Control," by Clayton H. Barnard, Application Engineer, Bailey Meter Co., presented before the Instrument Society of America National Conference, Philadelphia, Sept. 13-17)

CONTROL of modern continuous processes, with their more precise operations, can usually be handled successfully with the multi-element control systems, in which several variables are measured and coordinated to control a single function, or several functions.

The multi-element system is to be distinguished from the so-called "series" type of control, where several single element controllers are installed, each one measuring a single variable and in most cases controlling a single function.

Some advantages of multi-element control are stated as follows:

1—It overcomes the effect of process and transfer lag.

In any continuous process which is to be operated in equilibrium, the supply energy must at all times equal the demand energy, and the demand energy must be supplied at a suitable potential for the process, which may be expressed in terms of temperature, pressure, level, concentration or other terms. It is true that a measurement of potential is an approximate measurement of the ratio of energy supply to energy demand and in many cases it becomes an accurate measurement, in which instances single-element control will function successfully.

On processes having considerable process and transfer lag, the poten-

tial measurement no longer becomes an instantaneous measurement of supply and demand energy ratio, and poor quality control results. By actually measuring both supply energy and demand energy, and introducing control functions based on these measurements, the effects of process and transportation lag are eliminated.

Eliminates Uncontrolled Variables

2—Multi-element control eliminates the effect of uncontrolled variables.

In many processes, variables other than the one being measured have nearly as great an influence on the process, and cause upsets which cannot be corrected fast enough or accurately enough for precise control. By measuring and controlling from each major variable, the extraneous effects are eliminated.

3—Multi-element control eliminates inter-action between processes.

In some of the more complex processes it may be possible to control demand potential with fair precision, even though the instantaneous ratio of energy supply to demand does not remain constant. While this may be satisfactory for the particular portion of the process under consideration, the inter-action on other sections of the process make it undesirable in every case. By obtaining complete stability of the process through proper coordination of all major variables, these effects are eliminated.

4—Multi-element control provides inherent safety to processes which may become dangerous under poor control. Where processes have considerable lag and deviations in the ratio of supply to demand energy may become dangerous, a multi-element system will correct for the deviations before any serious conditions arise. A complete multi-element control system for refinery heaters, involving several measurements and the control of several functions, is shown in Fig. 1. The heater illustrated is of the vertical type having two parallel coils which must be controlled individually in order to compensate for coking and unequal distribution of the combustion gases which would have an effect on the balance of the heater. It is also necessary to maintain the temperature in the transfer line at a predetermined amount, and the rate of charge to the heater constant. It is also required to operate the heater at maximum efficiency and with complete safety, which requires the maintenance of the proper fuel-air ratio.

Charge Gives Basic Control

Basic control of the system is by an impulse from a measurement of charge flow, which regulates the two valves in the individual lines to the two coils and also provides the primary impulse for controlling the fuel and forced draft air. A temperature difference indicator is used as an index of balance of the two coils, and an impulse introduced through the two averaging relays as indicated to modify the setting of the flow control valves in such manner that flow through the two coils is unbalanced as necessary to maintain equal temperature leaving the heater. This modification does not in any way affect the total flow, as one valve is opened and the other closed.

Temperature of the oil in the transfer line establishes an impulse which is combined with the impulse from the charge flow controller through an averaging relay to supply fuel at the proper rate and also to modify the forced draft air supply.

An oxygen analyzer taking samples at the exit of the heater is used as an indication of fuel-air ratio, since it provides compensation for variations in the fuel supply. The oxygen recorder-controller impulse is combined with impulses from the charge flow controller and transfer line temperature controller to maintain the forced draft supply at exactly the proper amount for maximum combustion efficiency.

This system provides complete stability of the entire heater operation and also prevents interaction between preceding and succeeding processes. It overcomes the effect of process and transfer lag and provides for optimum safety. It is actually simpler than a series system consisting of a multitude of single element controllers each acting independently.

Rules for Applying Such Systems

Analysis of the above illustrations points to a few simple rules which can be used as a guide in applying systems of this type:

1—Measure each important variable in the process and from such measurement introduce a control impulse in such a way that it will influence the functions to be controlled in approximately the correct amounts.

2—Arrange the equipment in such way that the final measurement of energy potential has only to be a modifying controller.

3—When in doubt, use an impulse from the doubtful factor, since it can always be eliminated if found unnecessary, and the cost of providding for it in the original installation will be far less than applying it later if found necessary.

In general, the increasing use of end-product analyzers, as is typical in modern petroleum refineries, calls for multi-element control in view of the relatively large transfer and instrument lags involved, and the best application of such equipment is to use it as a modifying controller rather than as a primary controller.

* * *

EDITOR'S NOTE: Copies of the complete text of the preceding paper (No. 48-3-3) are available. See box, page 948.

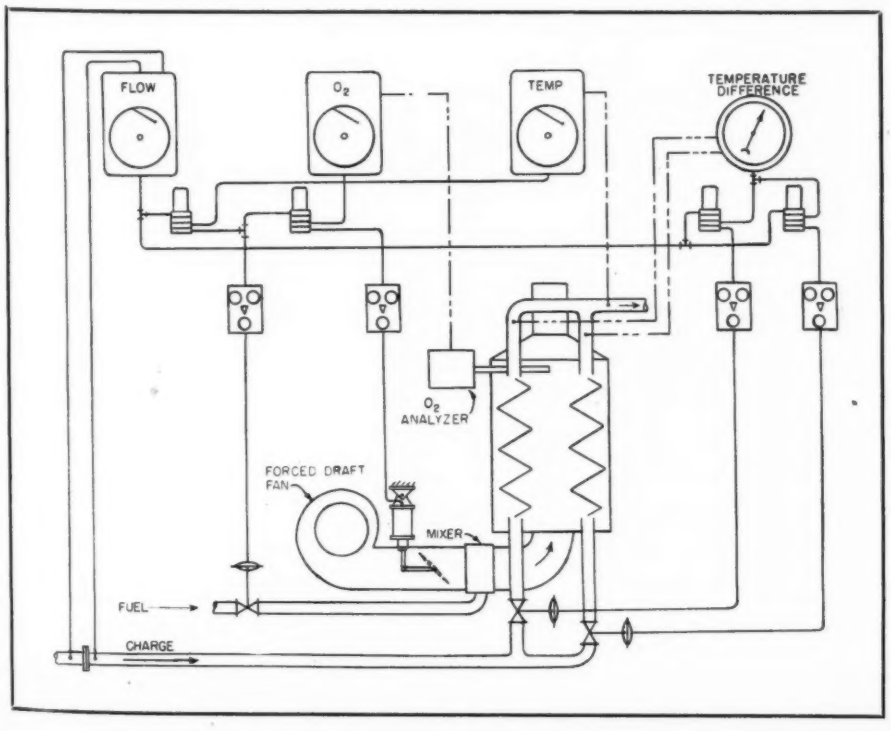


Fig. 1—Complete multi-element control system for refinery heaters

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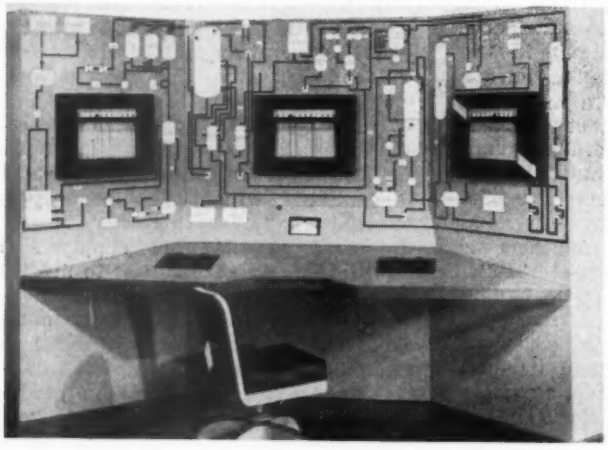

Fig. 1—Model of the console-type "Panel Board of Tomorrow." The flow diagram shown represents the principal piping for a fixed bed catalyst unit

Console Control Panel Overcomes Objections to Conventional Boards

(Review of paper entitled "Supervisory Control Systems," by Louis Gess, Chief Application Engineer, and Robert M. Hutchinson, Senior Development Engineer, Brown Instrument Co., presented at National Instrument Society Conference, Philadelphia, Sept. 13-17, 1948.)

TO overcome some of the objections to conventional instrument panels, such as their size and cost, time lag between observations by operators, and so on, a model console-type "Panel Board of Tomorrow", was built for demonstration to engineers in many industries.

The board makes finger tip control of the process possible by one operator, who has immediately before him an overall picture of the operation of the unit. Through the use of a special, pneumatically-operated system included in the processing unit instrumentation, called the "Remoteset," the panel board operator is able to change the set point of any remotely located control instrument in the unit. Fig. 1 is model of the panel.

The flow diagram shown represents the principal piping for a fixed bed catalyst unit. The multiple point strip chart recorder on the left records pressures, the center records thermocouple temperatures and the one on the right, flow and liquid level.

The small black dots on the model panel are lamps indicating points at which measurements are made. Each lamp lights as the corresponding record is printed. To the right is a bank of switches which permits the operator to select any recorded place of measurement, and connects its measuring element so that he gets intermittent or continuous indication on the indicator in the lower center of the middle panel. As a possible future development, the bank at the left would provide means for going on manual control, and means for remote setting of the control index.

The essential three components of the panel board are the strip chart recorder, the Remoteset mechanism and a pneumatic controller transmitter installed on the unit. These devices meet all the necessary requirements for supervisory panels; namely, a method for manually changing the set point of a controller located at a distance, and a means in the controller for transmitting measurements back to the board, where they would be both indicated and recorded.

The pneumatic system of the Remoteset operates on the null balance principle. Adjusting a set point indicator applies force to the top of a bellows. The movement of the bellows causes the supply valve to open and increases the air output pressure. Since the output air pressure is applied to the interior of the bellows, in opposition to the applied force, the valve will again close when the two forces are open. While this is occurring the transmitted output pressure is being applied to the setting mechanism in the controller, which moves the index to a new position.

Where accounting records are required, the transmitter controllers can be of the recording type; either multiple-pen instruments with circular charts or multiple point strip chart recorders.

* * *

EDITOR'S NOTE: Copies of the complete text of the preceding paper (No. 48-4-1) are available. See box, below.

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Abstracts of Other ISA Papers

"Valve Characteristics and Process Control," by N. B. Nichols and J. G. Ziegler, Taylor Instrument Co. (No. 48-2-1) This paper discusses the operation and requirements of the control valve, and its relation to the principle of automatic process control. An attempt is made to relate the "control valve characteristics" to the other factors of controlability.

"The Use of Interconnected Control Instrumentation for Offsetting Unfavorable System Characteristics," by J. A. Pellettere, Gulf Oil Corp. (No. 48-3-1) This paper presents an analysis of certain basic fluid-flow systems to assist in selection of instrumentation; a comparison of the characteristics of one-, two-, and three-function instruments with the characteristics of a multiple, or interconnected, system of instruments in cases where unfavorable time lags exist.

"Pneumatic Transmission Lag," by Mead Bradner, Foxboro Co. (No. 48-4-2) Data are presented on the characteristics and values of lags encountered with ¼-in. and ⅜-in. copper tubing in lengths up to 2000 ft., using "infinite capacity" inputs which were varied by (a) step upset, (b) constant rate, and (c) sinusoidal changes. A number of termination volumes were used.

"Organized Instrument Engineering," by J. Johnston, Jr., E. I. du Pont de Nemours & Co. (No. 48-5-2) This paper deals with the relative value of instrument engineering as a separately recognized department in the engineering organization of the instrument user. Discussion centers on the coordination between such a group and the research development, technical service, design, construction, operation, and maintenance departments of a given corporation. The author concludes by proposing what he considers to be the most efficient type of organization for this work.

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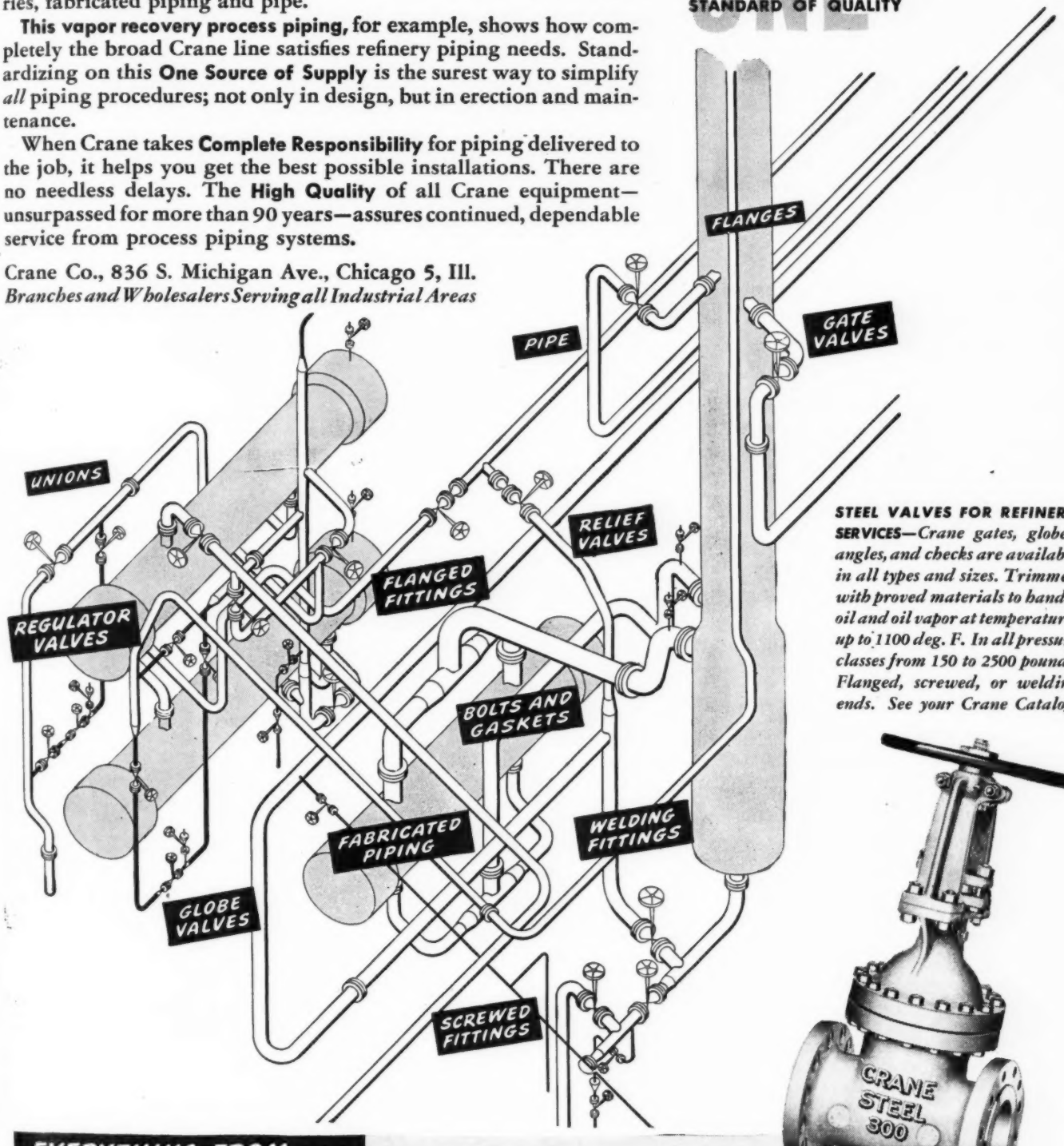

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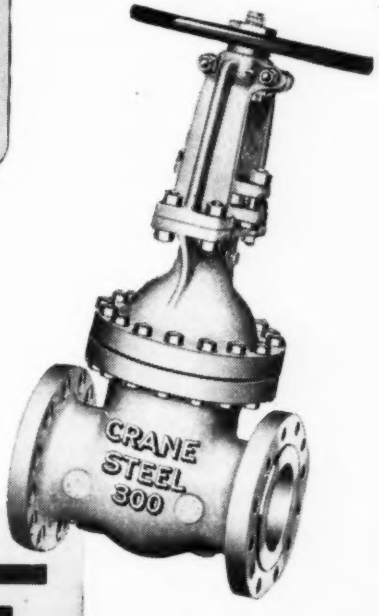

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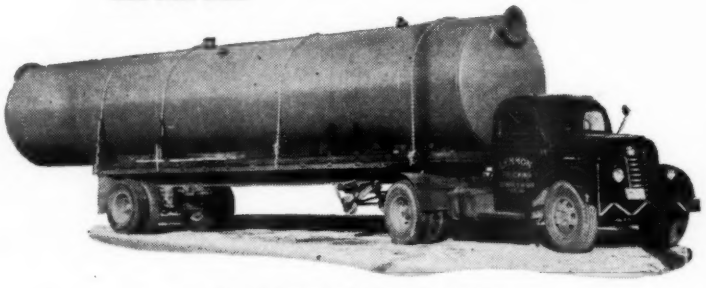

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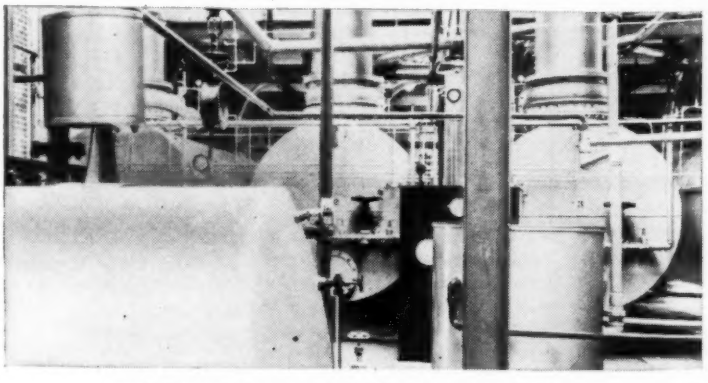

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Damage to Refractories and Tubes Results From Inefficient Furnace Combustion

Material in the accompanying article is taken from a paper entitled "Combustion and Efficiency," by High D. Wiant, Combustion Research & Development, Inc., Jersey City, N. J., and presented before the Regional Technical Meeting, Western Petroleum Refiners Assn., Wichita, Kans., June 11.

IN ADDITION to the paramount drawback of wasted fuel, inefficient combustion in a refinery furnace presents a number of other important and costly maintenance and operating problems. Among these are:

1. Refractories disintegrate rapidly and unevenly.
2. Tubes oxidize at an accelerated rate, becoming distorted.
3. Thermowells bend out of shape and become inoperative.
4. Capacity is reduced, as is on-stream time.

In explaining how poor combustion will damage refractories, it is stated, "If two refractories, each having different disintegration points, be placed in contact, the one having the higher disintegration point will be found to fail at approximately the same temperature as the lower quality material, surprising as this may seem. In furnaces where poor combustion exists, refractories show evidence of disintegration at a more rapid rate than those in furnaces having better combustion conditions. Evidently the carbon formed by inefficient combustion comes in contact with the refractory and lowers the disintegration point."

This condition is even more predominant in steam power plants, it is stated, where combustion chambers are much smaller and temperatures are higher than those normally found in oil industry furnaces. In most cases where walls and floor are being melted away, the slag will have a dark color when cold—evidence that another substance (presumably carbon) is combining with the refractory as it melts.

On the other hand, clean heat (no carbon) does not discolor refractories even in the molten state. High excess air rates, accompanied by high temperatures, can give trouble also. In that case, the slag or glaze remains the same color as the refractory.

This particular phenomenon has been noted also in catalytic cracking units, where the air heater combustion tunnel linings were glazed and decomposed to some extent. In each case, reducing the air rate stopped the melting in the lining. Although it is a common belief that a furnace can be operated at excess air rates to prevent decomposition of the walls, it is believed that what actually happens is improved combustion, thus eliminating or reducing the carbon which might come in contact with the refractory.

Another result of poor combustion is refractory failure from cracking and bowing, a common form being where the roof and nose tile fall out. This is due to uneven expansion and contraction, caused by some portions being heated more than others. The lips holding the tiles on the hangers are broken from the stresses generated. If the proper combustion conditions are maintained most of these failures would not occur. They are less noticeable in furnaces having tiles supported on hangers, because the tiles can shift more freely than with the other construction. If not corrected, this condition will lead to air leakage into the furnace, requiring more fuel, and eventually to draft difficulties.

Excess Air Promotes Tube Oxidation

When excess air is used, the uncombined oxygen in the heated gases is in a most active state. This frequently results in accelerated oxidation of the tubes, a condition often erroneously ascribed to overheating them because they are found bowed.

In one case the roof tubes of a crude coil bowed up, pushing both the tube hangers and roof tile out of place. The conclusion reached by the furnace owner was that the tubes did not have sufficient expansion allowances. If this decision was correct, the question is: why did *all* the tubes bow *up*?

"The one factor common to *all* tubes was that flue gas currents swept the undersides, and thus they were oxidized more on that side, after this attack commenced, the metal in the bottom side did not expand as much as did that in the top, thus forcing the tubes to bow upward over a several months' period. If there had been insufficient expansion allowance, the tubes would have bowed in a much shorter time."

Another example of oxidation is the bowing of thermowells installed in a verical position over the bridgewalls of a furnace. If these wells are oxidized to any extent, they also will bow, invariably *against* the flow of the flue gases. The same reasoning holds—the metal is oxidized on the side where the flue gases strike, and thereafter expands less than the unaffected metal. Likewise, wall tubes frequently bow out, horizontally. Any tube oxidized more on one side than another will bow in the direction from which the heat comes.

An illustration of what can be achieved without excess air is the case of the combustion tunnel of the flue gas generator of a catalytic hydroformer, fabricated of 18-8 stainless steel and approximately 0.125 in. thick by 3 in. high. This encircles the burners and literally sits in the fire, being cooled on the outer side by recirculated flue gases at approximately 800° F. Inspection of these cylinders after several months in service reveals little difference from original appearance; they are neither bowed nor warped. The reason these cylinders can give this service is because the generators are operated with less than 1% excess oxygen, and withstanding high temperature is all that is required.

Another example is the combustion tunnel in the air heater of a catalytic cracking unit. This is a carbon steel cylinder lined with firebrick, and on the end opposite the burner is an alloy ring exposed on one edge and side to the flue gases. This ring is located at the interface between flue

gases and air, and oxidizes very rapidly. Its best protection is the scale which forms; this should not be disturbed. Rapid oxidation occurs because the ring has to resist both high temperature and excess air.

Effects on Capacity and Stream Time

Analysis is made of what would take place in a furnace operated with a 45% excess air rate if this were reduced to 20%.

"First, the fuel rate necessarily would be reduced to maintain the same transfer line temperature. Second, the oil temperature outlet of the convection tubes would decrease. Obviously some of the duty previously performed by the convection tubes must have been transferred to the radiant section. Why?

"Even though less total heat is being liberated by the fuel fired, no fuel is required to heat the excess air which was eliminated. As a consequence of that elimination the flame becomes more radiant, resulting in more even heat distribution and increasing the efficiency. By reducing excess air, the volume of flue gases passing over the convection section is reduced and a lower oil temperature is obtained. The volume and the temperature of flue gases to the stack also is decreased.

"Obviously the slope of the oil temperature curve through the radiant bank is increased; therefore there is less danger of coke forming in these tubes. This increases stream time, especially on units charging a black oil or a stock with a high Conradson carbon."

Selecting New Equipment

The most important items to be considered when selecting new furnace equipment are summarized below:

1. The furnace firebox must provide ample combustion space, to secure sufficient heat transfer surfaces.
2. The stack must be large enough to remove the flue gases from the furnace and maintain adequate draft at the maximum load required. (This is one of the most abused items.) Usually stacks are of sufficient size to remove the flue gases if other conditions are retained. Draft difficulties generally can be eliminated by reducing excess air rate. This means also that leaks must be plugged, cracks repaired and inefficient burners replaced.
3. Refractories should be in good condition and not permit air to leak in; the importance of this cannot be overstressed. If fire boxes are sufficiently tight higher drafts can be maintained, permitting higher velocities through the air registers and allowing burners to be accelerated to much higher heat release rates with the same size registers.
4. The kind of fuel to be used determines the equipment necessary.
   (a) If gas is the fuel, a constant pressure should be available—usually 25 to 30 psi. is adequate.
   (b) If oil, a rotary pump should be used because it gives constant pressure and will crush solids small enough to pass the burners. A heater must be provided to reduce oil viscosity to a value permitting good atomization in the burner. A strainer is needed to trap out large solid particles.
   (c) If both gas and oil are to be used, either combination burners or interchangeable oil and gas burners must be provided.
5. The selection of burners and air registers is determined largely by the fuel used and will be discussed in detail.

Gas burners should be capable of performing satisfactorily with a minimum of excess air and without any flame enlargement in attaining that minimum. A gas burner which will permit the excess air rate to be reduced to approximately 15% before any sign of flame enlargement may be classed as a "good" burner. It should be capable of performing satisfactorily from 40 to 100% of maximum rating. Gas burners should have the characteristic of accelerating considerably; that is, when the fuel rate is increased, the flames will not increase in that proportion because tip velocity increases and combustion occurs more rapidly.

An oil burner with a low barrel or tip pressure usually is the best burner and pressure range should not exceed 20 psi. to avoid excessive tip velocities. The usual specification is steam consumption, lbs. of fuel per lb. of steam. Actually, this is improperly stated and should be: "steam consumption, volume per lb. of oil," for oil is atomized and carried by volume rather than pounds and the only possible way to lower barrel pressure is by increasing the orifices in the tip, thereby decreasing tip velocities.

The oil burner with the lowest barrel pressure will prove most satisfactory because the lower the velocity of the oil-steam leaving the burner tip—still keeping the oil atomized—the more time the oil has to vaporize. The more vaporization, the easier the burner is to light and keep lighted. A good one always will ignite close to the tip. Oil burners with high tip velocities increase the flame length and often squirt oil all over the firebox. Such burners are difficult to light and keep lighted. V-port types of cocks or valves are most suitable for controlling flows of oil and atomizing agent.

The selection of a combination oil and gas burner involves more considerations than for either fuel alone. In selecting the burner, the first objective is to choose the one giving the best result (and the simpler the mechanism the better). Second, the convenience of switching from one fuel to the other should be considered. Third, the burner should be easily adjusted. Fourth, effect of switching fuels on the furnace conditions should be evaluated. Last, the ease with which burners can be removed for maintenance should not be overlooked.

Operator Training

One of the most important factors to stress about operating burners is independent of burner make and type; it is operator training. Failure here can render the best possible burner or furnace inefficient.

It is an unfortunate fact that the men operating and firing furnaces often have limited knowledge of combustion and what occurs in a furnace. Fully half of them do not know the importance and functions of the draft; it never enters their minds how they get it, or that there is a limit to the capacity of a stack. They do not realize that air leaking into the furnace has to be removed by the draft created by the stack and that this means excess air in the furnace, which increases the load on the stack.

Even if a furnace is being operated under pressure and burner flames are excessive, the common expression is that registers are "too small." Many operators do not realize that even with larger registers there will not be an increase in air flow to the burners. Most firemen erroneously believe more heat is being released with an increase in the size of the flames.

Finally, for the best results, the maximum cooperation among purchaser, vendor, and operating personnel is necessary with any combustion equipment.

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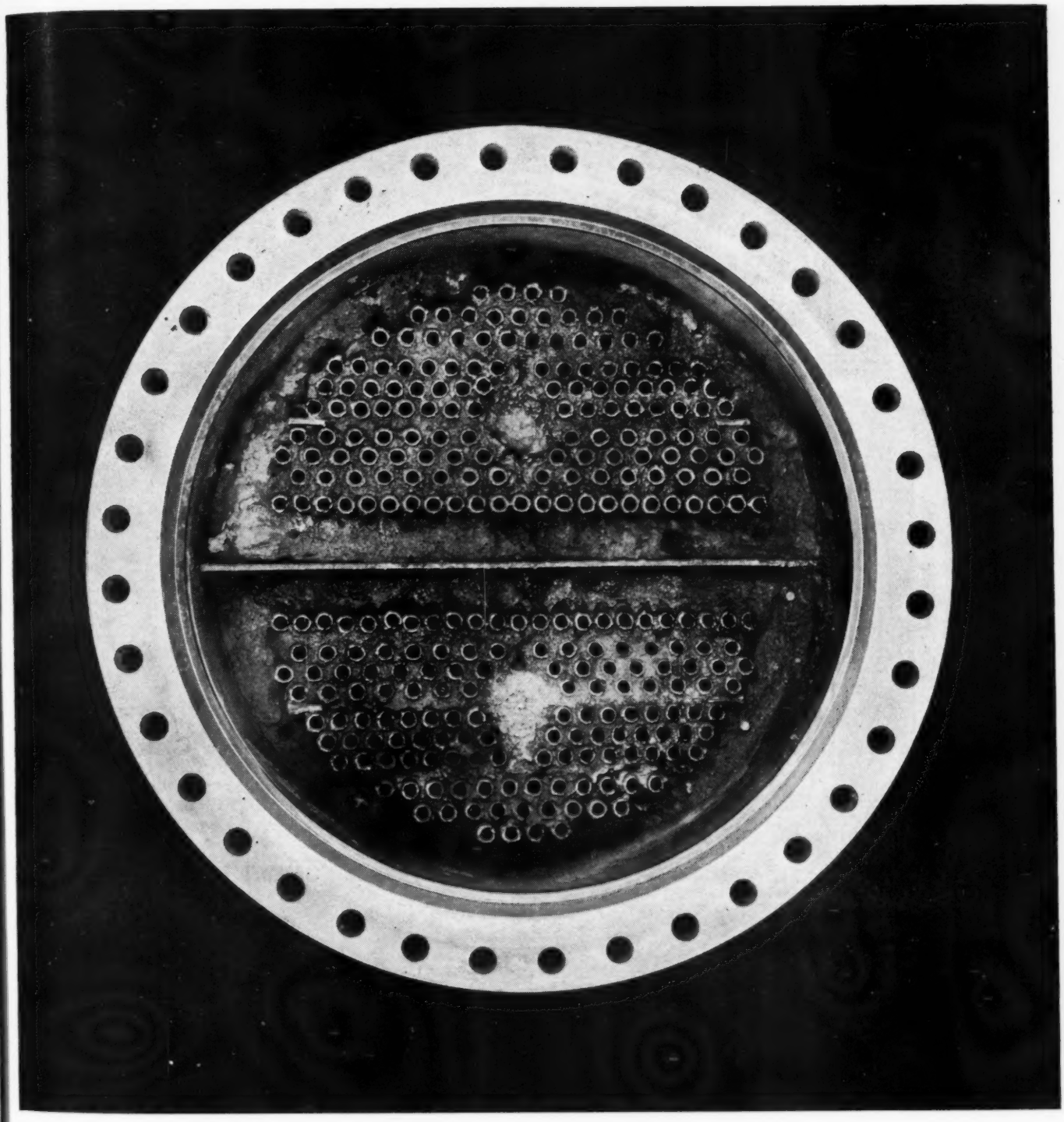

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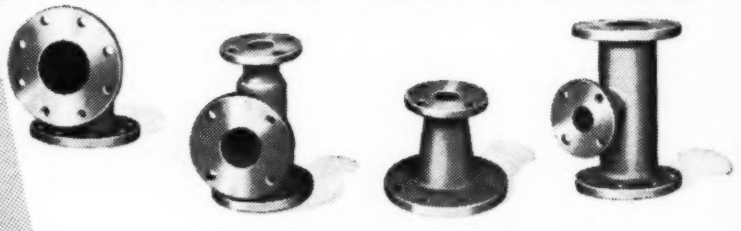

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C 17	Cr. 18%, Ni. 8% C. Max. .20%	Tensile St. Yield Pt. Elong. 2 in. Red. Area Brinell Wt. per cu. in.	85,000 psi 45,000 psi 50% 50% 165 .28 lb.
C 17 S	C. .07—.10%		
C 17 SMO	C. .07—.10% Mo. 3%		
C 17 SCB	C. .07—10% Cb. .70%—1%	Tensile St. Yield Pt. Elong. 2 in. Red. Area Brinell Wt. per cu. in.	90,000 psi 60,000 psi 30% 35% 180 .28 lb.
C 22	Cr. 24—28% Ni. 9 —12% C. .20—.50%		
C 22 S	C. .10% max.		
C 25-20	Cr. 24—26% Ni. 19—20% C. .20—.30%	Tensile St. Yield Pt. Elong. 2 in. Red. Area Brinell Wt. per cu. in.	65,000 psi 45,000 psi 22% 25% 180 .29 lb.
C FA20	Cr. 19—21% Ni. 28—30% C. Max. .10% Molybdenum 3—4% Silicon 1.5% max. Cu. 4-4.5%	Tensile St. Yield Pt. Elong. 2 in. Red. Area Brinell Wt. per cu. in.	75,000 psi 45,000 psi 40% 45% 140 .29 lb.
MONEL (MM)	Ni. 67% Cu. 28% Fe. 3% Si. 1%	Tensile St. Yield Pt. Elong. 2 in. Red. Area Brinell Wt. per cu. in.	65,000 psi 33,000 psi 25% 28% 150 .32 lb.

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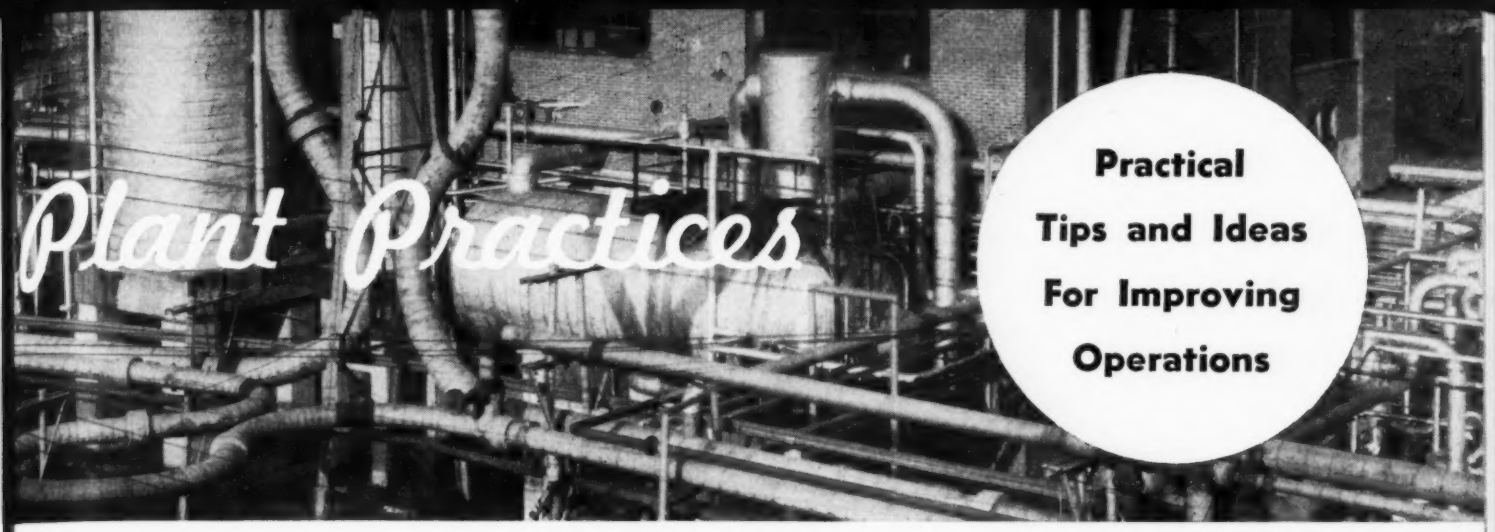


Australians Separate Pipe Flanges Quickly By Using "Slip" Flanges and Jacking Bolts

By A. M. JOHNSON, Installation Superintendent
Commonwealth Oil Refineries, Ltd., North Fremantle, West Australia

USE is made frequently in our refinery of a number of "slip" flanges, also sometimes called "spectacle" flanges, for cutting out portions of various transfer lines between tanks and/or processing units. A permanent installation between a pair of pipe flanges, the slip flange comprises a combination open and blind flange, as illustrated in Fig. 1. It is cut generally from mild steel plate. In the case of an 8-inch size it may vary from ¼ to 1 in. in thickness. It is not intended to replace a valve, but rather to supplement it.

In the past, considerable time and manpower was needed to separate the pipe flanges; in fact, it was often necessary to play fire hoses on the piping to contract them. A simple method for jacking the flanges apart has now been devised and adopted as standard practice. It is as follows:

The pipe flanges are 8-in British Standard Table "H" (indicating 14½ in. diameter, 1¼ in. thick, and drilled with 12 ⅞-in. bolt holes). Any convenient bolt hole is selected and tapped through both pipe flanges. The equivalent common hole in the slip flange is then drilled out to 1-1/16 in.

When it is required to swing the blank, or slip flange, all bolts are removed and two bolts, threaded to fit the tapped holes in the pipe flanges, are screwed in, one from each side, as shown in Fig. 2. These bolts are set so as to meet half-way through the slip flange, and are then tightened against each other, jacking the pipe flanges apart. The slip flange is then swung to the blind position as in Fig. 3, pivoting around the jacking bolts.

New ring gaskets are fitted if necessary, and the jacking bolts are slackened off, allowing the pipe flanges to come together, the blind position of the slip flange being retained. When it is desired to return the piping to flow operation, the procedure is repeated, swinging the slip flange back to the open position in the same manner employed in closing the line in the first place.

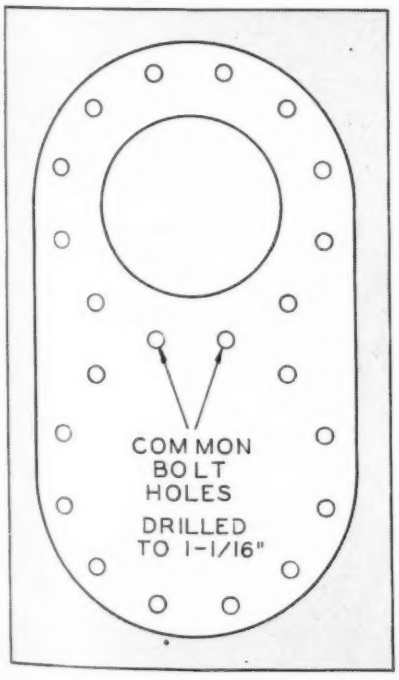


Fig. 1—Eight-inch "slip" flange, usually mild steel plate, the thickness depending upon the service for which it is intended

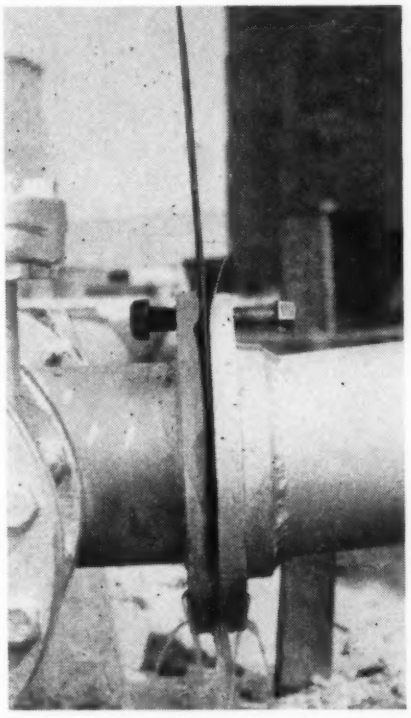


Fig. 2—Slip flange ready for swinging; all flange bolts are removed, and two jacking bolts in position

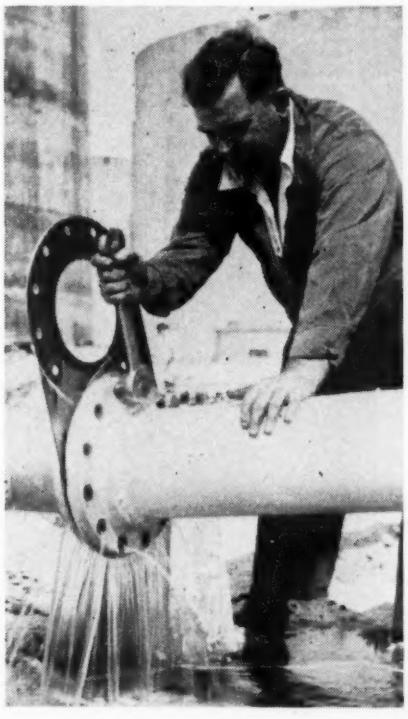


Fig. 3—Pipe flanges have been jacked apart, allowing slip flange to be swung into blank position

Metal-covered Carrier Safe Replacement For Conventional Asphalt Sample Cans

By JOHN C. ALBRIGHT

A CONVENIENT carrying case for hot asphalt samples that will afford complete protection for the sample taker can be made quickly and easily by the plant tinsmith. This case is constructed of light gage sheet metal with a compartment on each side of a tall carrying handle so as to balance the load. It is illustrated in the sketch, Fig. 4.

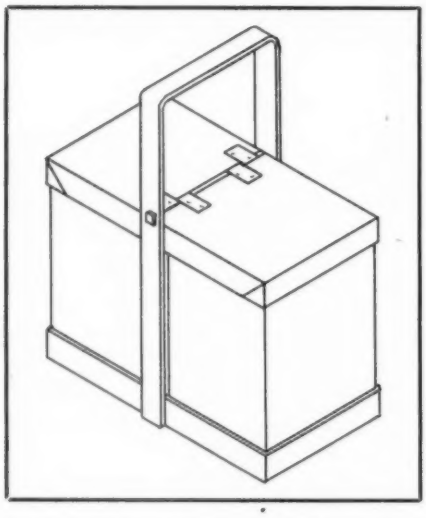


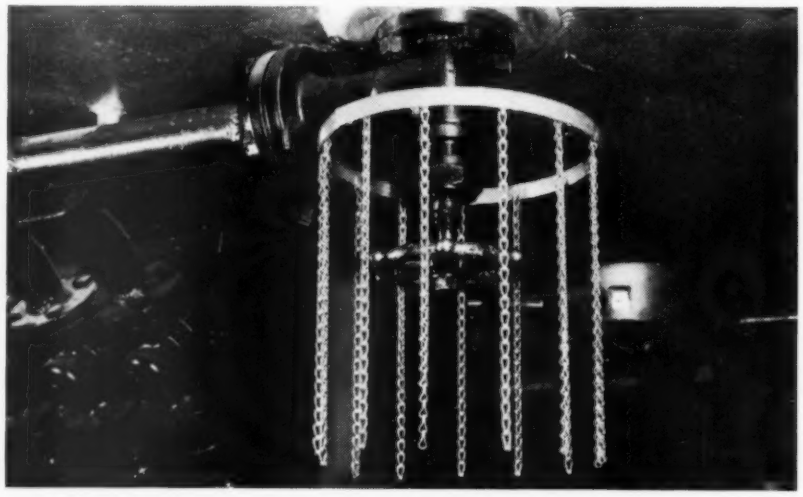
Fig. 4—Union Oil Co.'s safe sample carrier for hot asphalt

The size can be of any dimensions, but when standard square cardboard sample cups are used, it should be designed so that the rimmed base will hold the filled carton snugly. Rimmed lids with hinges attached to a cross bar between the legs of the handle are heavy enough to drop of their own weight down over the open ends of the cartons and prevent splashing of the hot liquid.

The sample carrier was developed by workers at Union Oil Co. of California as a replacement for conventional metal cans with soldered-on bails, because the temperature of the sample was frequently high enough to soften the solder and cause the joint to separate, spilling hot asphalt on the employes.

Borrow Railroader's Safety Stunt

By ROGER TRENGOVE, Grease Maker Foreman
Continental Oil Co., Ponca City, Okla.



AS A WARNING to men walking the tops of trains of cars with their backs to the direction of travel, railroads hang cords from overhead supports a short distance ahead of tunnels, low bridges, and other hazards.

Borrowing this railroaders' idea, Continental has hung cords or chains around potential "head bumpers." When a person raises his head under an obstruction so protected, he will hit this warning first and instinctively duck his head. These warnings can be used on all kinds of low clearance obstructions, valves, lines, beams, and so on.

IDEAS—Wanted!

Plant operators, foremen, engineers, superintendents!—Send in your own original contributions on "how we do it around the refinery."

Material submitted for publication exclusively in PETROLEUM PROCESSING is paid for at the usual space rates. The idea is the thing—we'll dress it up.

Plant Practice Editor
PETROLEUM PROCESSING
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Test Houdry Valves for Leaks At Rate of 36 per Day

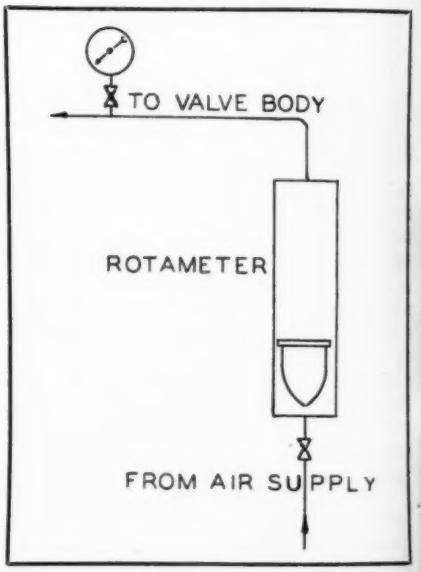
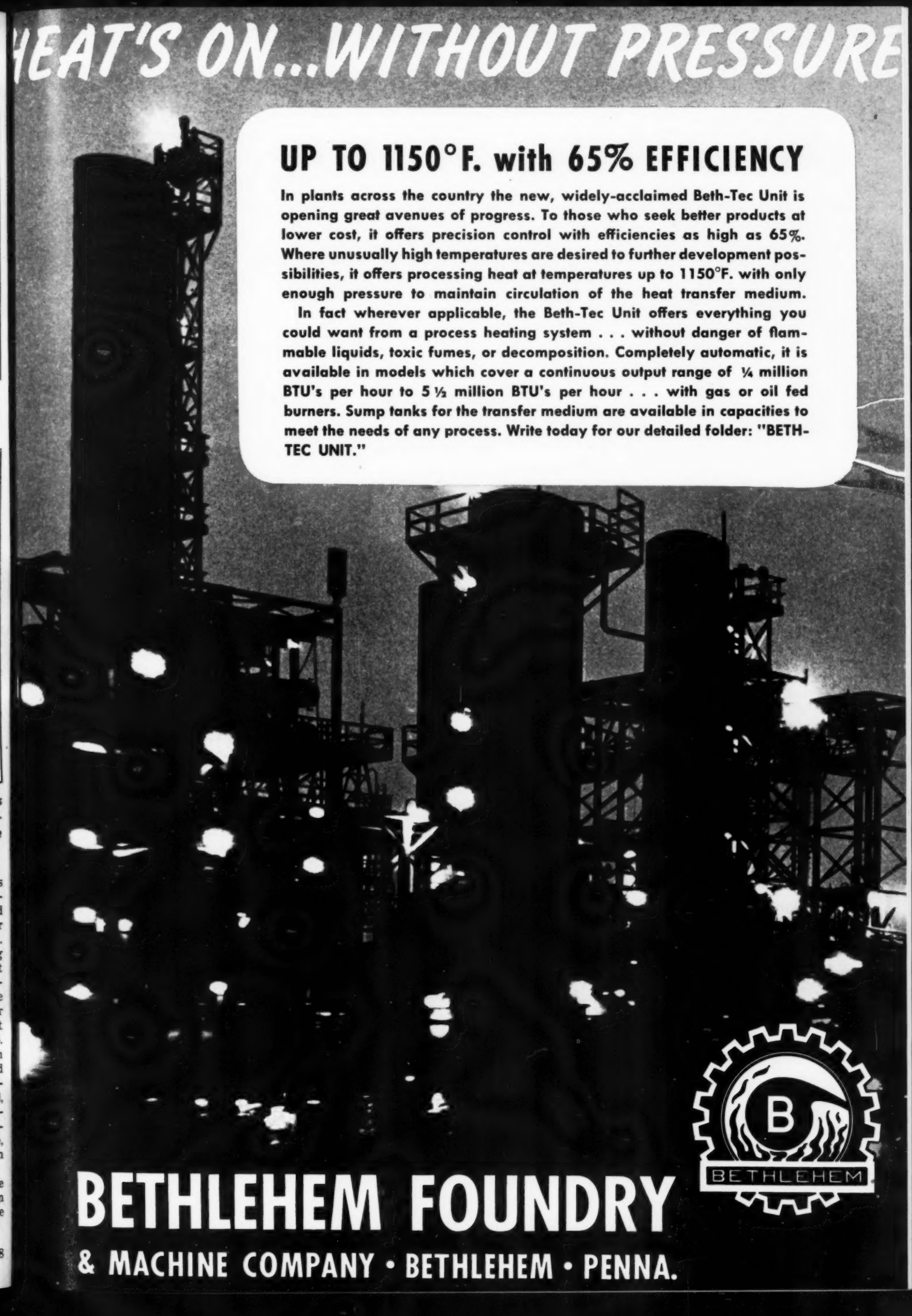


Fig. 5—Arrangement used by inspectors at Socony-Vacuum's East Chicago refinery for testing for leaks in large Houdry unit gate valves

LARGE motor-operated gate valves in Houdry units must be leakproof at all times to assure safe and proper operations. There must never be any leakage of the blocking steam. For quick and positive checking against such leakage, engineers at Socony-Vacuum Oil Co.'s East Chicago refinery use a simple scheme involving the plant's compressed air system and a rotameter flow gage. It is illustrated schematically in Fig. 5.

The air line is connected through the rotameter to the valve body, and the air valve is opened. Once equilibrium in pressure has been reached, any slight leak will be indicated immediately by flow as shown in the rotameter. The test is not quantitative, therefore no readings need be taken on the gages.

Socony's inspectors have been able to test all 24 valves on one unit in about 4 or 5 hours, for an average rate of about 36 valves per shift.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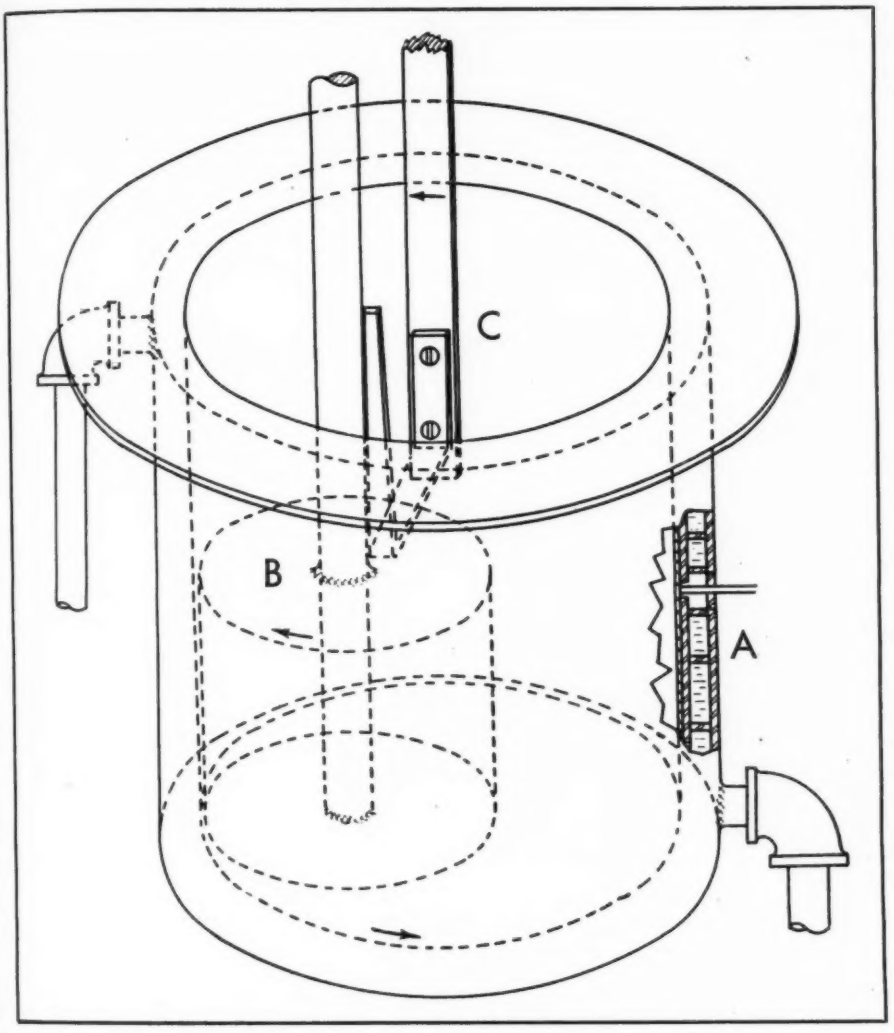

Fig. 1—Texaco's improved laboratory grease kettle

MANY types of lubricating greases can be quickly and easily prepared in small quantities for laboratory study in a small, oil-heated kettle being used at the Beacon, N. Y. research laboratories of The Texas Co. Developed by Texas Co. engineers, the kettle is said to cut the time required to make lubricants for research and testing. By permitting close temperature control, it provides a high degree of accuracy in reproducing products. By eliminating a draw-off valve, all possibility of loss of ingredients or contamination of the grease by remnants of previous batches is avoided.

The conventional steam-jacketed kettle used in preparing greases in the laboratory stirs less effectively than the new design, allowing channeling of stiff grease bases and producing poor mixing and uneven heat distribution, faults which must be avoided to obtain accurate results.

As illustrated in Fig. 1, the new four-liter kettle is stirred by a pestle (B) which moves with a planetary motion, reaching all parts of the interior. The kettle is heated by an oil jacket (A) and is insulated with magnesia to insure precise temperature control.

A scraper (C), running in contact with the wall one-fourth of a revolution behind the pestle, avoids "dead spots" on the kettle wall above the pestle and on the pestle itself. A cross arm of the scraper sweeps both the pestle top and the lower part of the pestle shaft.

The new device is a flat-bottomed cylinder, 8 in. high and 8 in. in diameter, lined with 14 gage stainless steel inside the oil jacket, and insulated throughout with magnesia. The pestle, a stainless steel cylinder $5\frac{1}{16}$ in. in diameter by 4 in. in height, is mounted on a 1 in. shaft. It moves around the kettle at 18¼ rpm., and rotates on its shaft at 60 rpm., resulting in a shearing motion at the kettle wall of 8 in. per second. Clearance between the pestle and the kettle walls and bottom is $\frac{1}{16}$ in.

Heating is provided by pumping pre-heated oil through the jacket on the kettle sides and bottom. Temperature is measured by a thermocouple which passes through the jacket to the outer surface of the stainless steel liner. The kettle is mounted so that it can be tilted to remove finished products. During this operation, the pestle and scraper unit is removed. Swing joints on the connections prevent damage to the pipe system.

"Draft Stoppers" Improve Viscosimeter Operation

WINDOWS in the physical inspection room of Sinclair Refining Co.'s East Chicago refinery laboratories face a wintry blast for the major portion of the cold weather season.

Heavy and intermittent drafts of cold air gave laboratory technicians trouble in running viscosities because the bank of Tag-Saybolt viscosimeters are all located along a bench in front of these windows and directly in the path of the draft.

Limited space in the building allowed no other location for the viscosimeters, so the problem was solved by building a set of glass and metal barriers to serve as "draft stoppers," one of which is shown in the sketch in Fig. 2. Each unit consists of a metal framework holding four panes of glass, and built to a shape to partially envelope the viscosimeter.

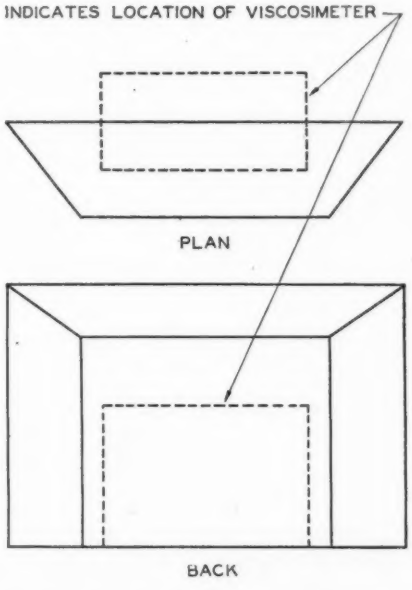

Fig. 2—Simple "draft stopper" used at Sinclair's East Chicago refinery laboratory

Assemble Safety Valve for Vacuum Still From Stopper and Ground Glass Joint

A simple safety valve for a vacuum still to guard against sudden pressure surges such as occur when "bumping" develops, can be made by an amateur or professional glassblower and attached to the usual design of laboratory fractionating column by an inverted glass "tee" in the vacuum line.

The device is illustrated in the drawing in Fig. 3, which assumes a vacuum take-off in the column head above the reflux condenser. Cork *A* is of any desired material to avoid contaminating still contents, although cork or rubber is commonly used; *B* is the male portion of a ground joint larger in inside diameter than the minimum diameter of the cork, sealed to the vacuum line to make the stem of the "tee"; *C* is the female portion of the ground joint, and is open to the atmosphere or, preferably, the laboratory vent system.

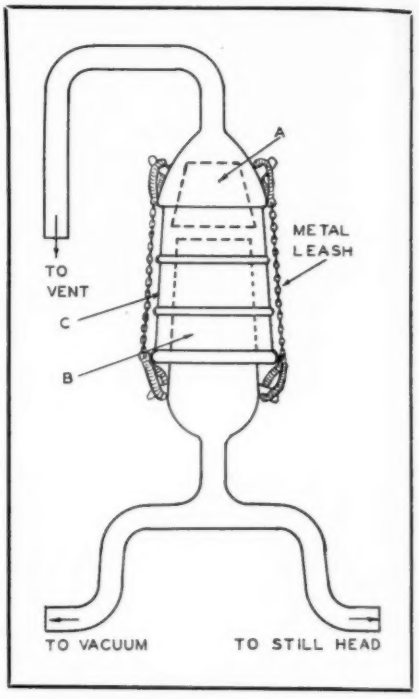

Fig. 3—Design for an automatic safety-release valve to guard vacuum stills against sudden above-atmospheric pressure surges

The glass cap *A* over the cork must be enough larger than the maximum diameter of the cork to permit sufficient clearance for ready release of pressure, but an excessive difference must be avoided so that the cork will seat readily. A difference of a few millimeters in the respective diameters is usually sufficient. Also, the end of the stem on the "tee" at *B* must be flat, to afford a seat for the cork. Minimum diameter of the cork must be large enough so that it will seat without necessarily being centered over the stem of the "tee". The joint is held together by metal "leashes" as shown.

This safety release operates whenever a surge of above-atmospheric pressure occurs in the still and column, automatically re-seating itself when the surge is over. It has successfully prevented damage to the distillation assembly when severe "bumping" occurred on operations where, with unequipped stills, thermometers were shot across the room, and corks and ground joints were blown out. Located above the reflux head or near the product receiver, there is little danger of damaging the distillation train or getting enough air following a "bump" to cause concern.

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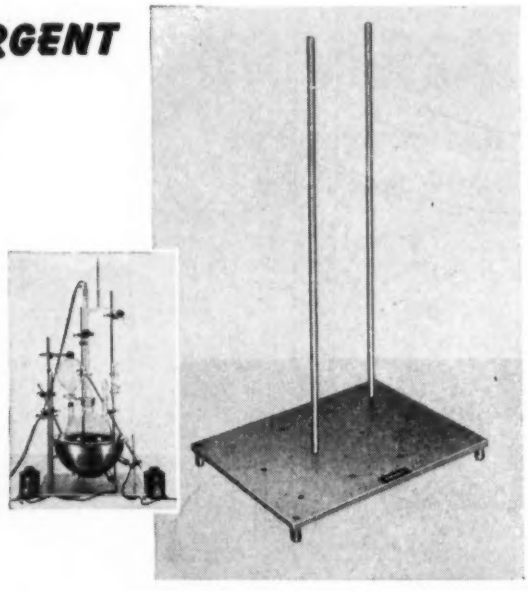

Recognizing the inconveniences which are encountered in using conventional type support stands for setting up assemblies in the laboratory, E. H. Sargent & Co. has devised a new assembly support system which eliminates these difficulties and provides the chemist with a highly useful base on which to carry out any bench operation.

Consisting of a heavy gauge aluminum plate, available in two sizes, supported by four adjustable feet, for leveling, and tapped and threaded at convenient intervals to receive stainless steel rods, this new support stand has qualities of stability, rigidity and flexibility of application not found in other conventional type stands.

The stainless steel rods are threaded at one end and tapped at the other, giving the operator a variety of heights in one foot increments as well as a wide selection of lateral distances at which the rods may be placed. For setups having large lateral distances two or more of these bases may be locked together by crossbracing an upright on one to an upright on another. Any conventional clampholder of sufficient size to fit the rods will work satisfactorily.

The new Sargent Assembly Support System offers a common level base with heavy steel rods on which a wide variety of assemblies may be constructed and held rigidly in place.

For your convenience in preparing an initial order, we have grouped under the following catalog numbers, such of the component parts of the system as we believe will be adequate for general laboratory use:

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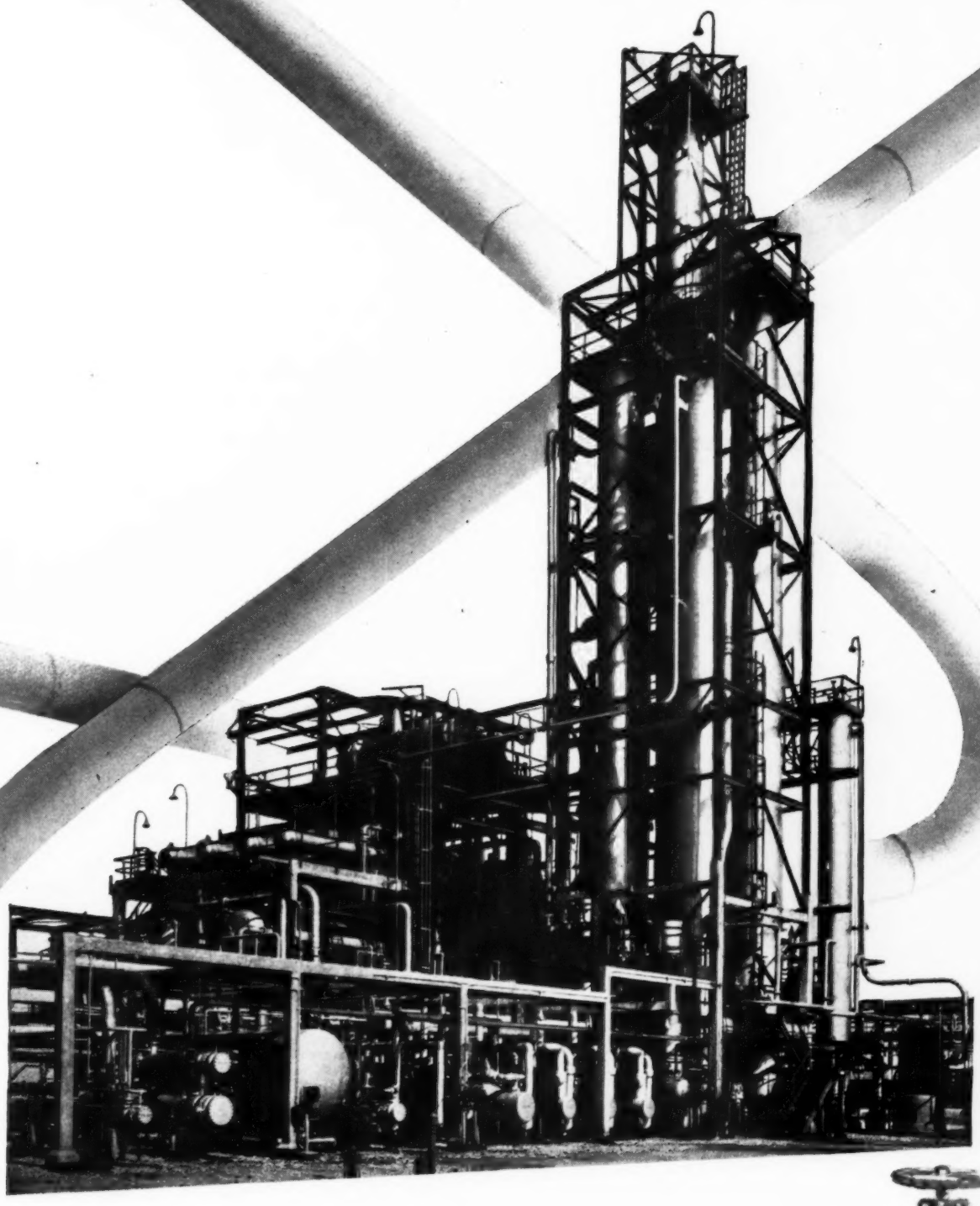
Jefferson Chemical's ethylene plant—



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high yields of Ethylene from varying charge stock compositions

Large ethylene plants are much like big petroleum refining units.

An ethylene plant must be designed for high yields, varying charge stock compositions, economical operation and minimum investment costs. Fundamental design must take a long term view of the plant—ease of operation, long on-stream periods, minimum turnaround time and low maintenance costs.

Long range thinking, good engineering, careful planning by Jefferson Chemical Company and Lummus are reflected in the performance of this ethylene plant at Port Neches. This plant is producing high yields of ethylene from varying charge stock compositions. When shut down for scheduled inspection after five months initial run, turnaround was completed in about fourteen days. Examination showed equipment to be unusually clean and in good mechanical condition.

Playing an important part in the high yields of this ethylene plant are the Lummus Cracking Heaters, especially designed to obtain required temperature-time relationship with minimum coke deposition. On-stream periods of two months have been obtained and there are good possibilities of extending these periods.

Including an ethylene plant now under construction, Lummus has designed four plants for the production of ethylene from petroleum, with a total capacity of approximately half million pounds per day.

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NATIONAL PROJECT CONTRACTORS ASSOCIATION — OIL STEEL CHEMICAL

Fuels for High Compression Engines Are Evaluated for Chemical Society

A STAFF REPORT

By the Editors of Petroleum Processing

VALUABLE data on the chemical side of high-octane gasoline manufacture, and on the requirements for these fuels in high compression engines, was presented before the Division of Petroleum Chemistry, at the American Chemical Society's 114th meeting in St. Louis, Sept. 6-10.

Another topic of interest to refiners was a series of papers dealing with the preparation, characteristics and uses of chlorinated and fluorinated hydrocarbons, many of which either are or can be synthesized from petroleum.

Considerable economies in operation as well as in octane requirements could be achieved by correcting the maldistribution of both fuel quality and quantity in multi-cylinder engines, it was brought out in a report on an investigation by Sun Oil Co. The work, described by R. W. Donahue in a paper "Multicylinder Engine Distribution," was done on a single engine, but the data are said to be in good agreement with that of previous investigators. The research project was undertaken specifically to study the fuel factors affecting distribution, rather than general engine performance.

While it has been known for some time that certain cylinders in an engine receive richer fuel mixtures than others, as was confirmed by this investigation, it also was found that the octane rating of fuel burned in individual cylinders varied widely. Fuel volatility often has been blamed for maldistribution problems, but this research showed the effect to be only a minor one.

It was found that the front half of the engine received a comparatively lean mixture, due to the effects of engine speed, inlet air temperature and deflection patterns of air and fuel in the carburetor. The effects of speed were found to be relatively small over the range, but higher speeds improved quantitative distribution. Higher inlet air temperatures likewise had a small improving effect on distribution. By comparison, quite large changes in distribution were produced by apparently minor alterations in the intake system, such as operating with the choke closed a degree or two or rotating the carburetor 180° from normal position.

In analyzing samples taken directly from the combustion chamber just ahead of the spark, it was found there also was a wide variation in fuel quality at this point. Two fuels were used in this test, one having components relatively constant in quality over the boiling range, while the other had quality variations of as much as 50% over the boiling range. When the first was used, the maximum octane spread between cylinders was 1.5 numbers; the spread was about 8 numbers with the second.

It is pointed out that refiners can do nothing about maldistribution as result of the directive effects of the carburetor, and that fuel volatility is not an important factor. Balancing fuel quality for uniformity over the boiling range is worthy of refiners' attention, however; since, if one or two cylinders are starved octanewise and knock, to the customer the engine will apparently demand a higher octane fuel than it really needs. In either case a conservation of fuel supplies will be achieved.

14 Blended Gasolines Studied

In "A Preliminary Study of the Octane Performance in High Compression Engines of Gasoline Prepared by Selective Blending of Gasoline Distillates from Present-Day Refining Processes," W. E. Offut, J. E. Taylor and G. B. Swartz, Jr., Gulf Research & Development Co., reported results from studying 14 fuels containing gasolines and distillates from "normal" refinery stocks and blended with other fractions made by cutting and cross-blending in the gasoline boiling range. These were tested in experimental high compression engines requiring approximately a 93-Research octane fuel and in conventional engines equipped with special high compression heads. Compression ratios ranged from 8:1 to 12.5:1.

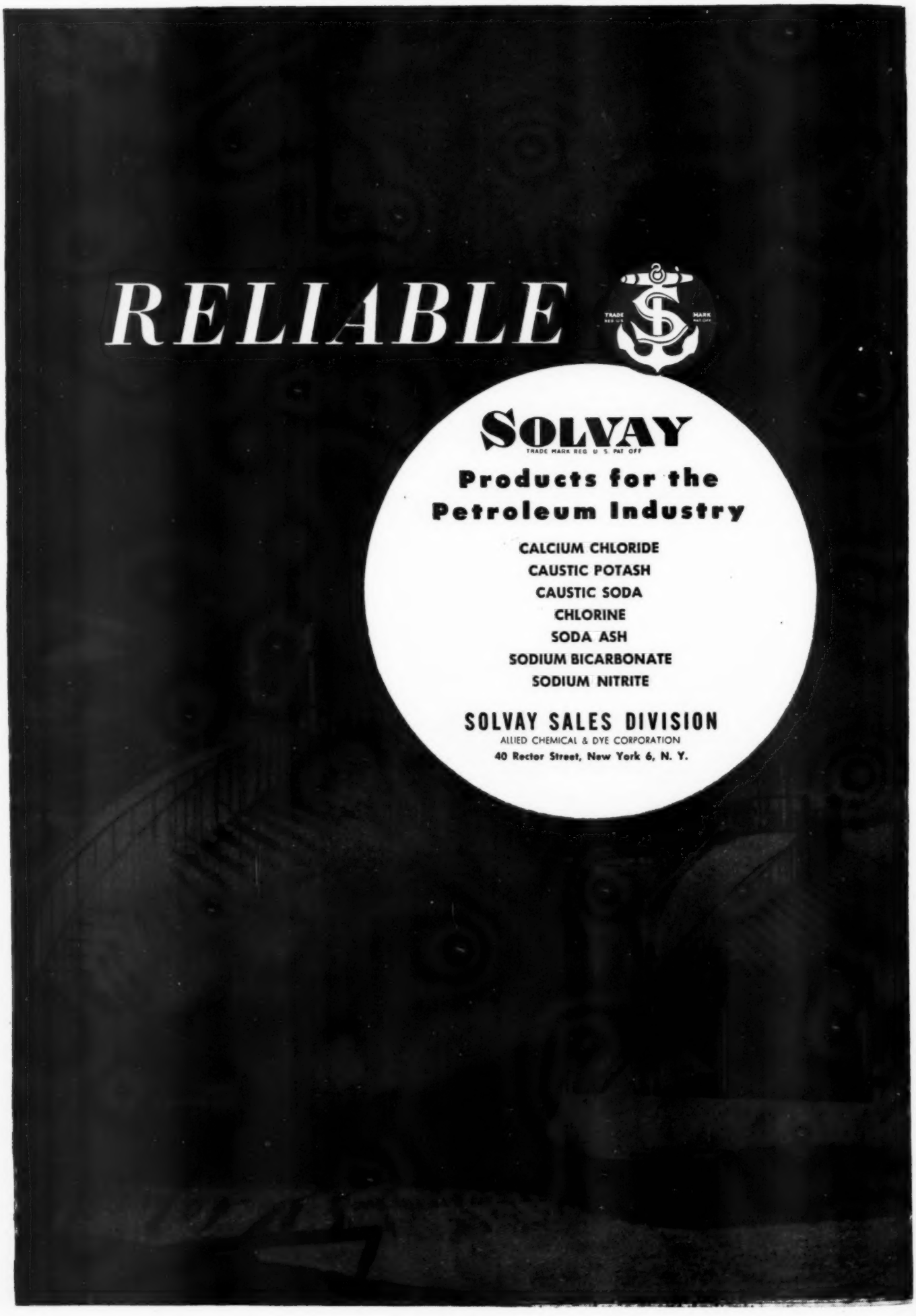
The Road knock ratings of the fuels tended to become higher as compression ratio was increased in the experimental engines. At 1200 rpm Research ratings were fairly close to the Road ratings; at 2800 rpm, where Motor ratings usually correlate closely with Road ratings in today's engines, the Motor rating was below the Road rating at 8:1 compression ratio, and this deviation became increasingly greater, although at a lesser rate, as ratios were increased. The data also revealed that the stepped-up conventional engines rated the experimental fuels lower than did the specially-designed high compression engines, particularly at high speeds.

In view of the small number of fuels used and relatively limited data, observed results of changing hydrocarbon composition are considered as indications rather than conclusions. However, these data indicate that replacing olefins, paraffins and naphthenes in the 200-325° F. fraction with aromatics increased particularly the low speed Road rating but also gave a noticeable effect over the entire speed range. By substituting paraffins and naphthenes for heavy olefins an increased high speed Road rating was obtained. By increasing aromaticity and leading to the desired Research rating, the effect of light olefins was apparently canceled. Fuel volatility decreases did not seriously reduce Road octane, but resulted in a performance loss other than octanewise which was not measured quantitatively.

The authors conclude that future fuel development programs should be carried out in engines of the specific design to be used on the road and that Road octane rating increases with compression rating. Correlations between Research and Road ratings appear to be significantly better in the high compression engines than those obtained with commercial gasoline in today's engines.

Also Studied Compression Ratio

In a similar study of "Antiknock Quality Requirements of High Compression Engines", by R. W. Scott,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G. S. Tobias and P. L. Haines, Standard Oil Development Co., 16 experimental fuels were evaluated in four high compression automobiles and two having engines of conventional design equipped with high compression heads.

Here again it was found that octane requirements increased with compression ratio, but that the increase becomes smaller as the higher compression ratio levels are reached. Further, the Motor octane requirement increases at a lower rate than does the Research requirement, implying that the Motor octane number becomes less important and fuels having a higher "jump" can be tolerated before high speed knock becomes limiting.

This conclusion is extremely important to refiners, since the processes that could be utilized, such as catalytic cracking and poylmerization, give fuels of high octane rating and with a high "jump," or sensitivity. If the reverse were true and low "jump" fuels were required, it would be necessary to use more expensive and restrictive processes than those currently available to produce these fuels. The laboratory octane number requirements given in Table 1 are based on sea level operation, in terms of Research and Motor ratings.

TABLE 1—Engine Octane Requirements

Compression Ratio	Research Rating	Motor Rating
7.5:1	89	77
8:1	93	78
8:1	93	78
9:1	96	82
10:1	99	82
12.5:1	102	84

Correlation of Road, "Lab" Ratings

An investigation of correlations between Road antiknock rating and laboratory ratings obtained by the Research and Motor methods was undertaken by J. B. Duckworth, G. T. Moore and C. J. Domke, Standard Oil Co. (Ind.) to demonstrate how customer preference may be expressed in terms of laboratory knock ratings and to review previous data on the subject. A study of customer habits and choices indicated a preference for fuels having relatively high Research ratings, largely because of their ability to suppress knock at low-speed full-throttle conditions.

In this investigation 300 fuels obtained from Midwest and Eastern service stations, were tested plus 75 special fuels designed to cover the gaps in grouping the commercial fuels; Research octane ratings ranged from 75 to 95 and Motor ratings, 68 to 83. By plotting Motor octane and Research octane vs. the Road knock rating in conventional engines, it was reconfirmed that little correlation between Motor and Road ratings exists, while based on a statistical treatment of the data, correlations were obtained between Road and Research ratings giving an average deviation in Road units of plus-or-minus 1 and with a maximum deviation of 5.8 units. By applying a correction based on Motor rating to the Research rating at low speeds, accuracy was improved to 0.9 Road units, while maximum deviation dropped to 4.5 units.

For new engines and new type fuels, however, the authors cautioned that these should be evaluated in highway service until it is determined what correlations may then apply between laboratory and service conditions.

How Processes Affect Output

A study of refining operations was reported by A. A. Draeger, G. T. Gwin, C. J. G. Leesemann and M. R. Morrow, Humble Oil & Refining Co. in "Production of High-Octane Gasoline Components," wherein the various gasoline manufacturing processes were described and their application reported in the commercial processing of a typical crude. The selections of the processes were arbitrary to show effect of sequential addition of processes and are given as an example.

By employment of the various processes indicated it was shown possible to increase total gasoline yield from 25% for straight-run distillation to 61% (on crude); the effect of manufacturing 13% of Grade 100/130 avgas is shown to decrease automotive gasoline yield to 47%. The data in Table 2 are calculated on the basis of maintaining a reasonable production of other refinery products in "normal" quantities.

Production, Use of Hydrocarbon Halides

Introducing the symposium on petroleum chemicals containing chlorine and fluorine, Dr. Gustav Egloff, Universal Oil Products Co., brought out that 75% of the 1,500,000 tons annual U. S. chlorine production currently is being used in organic chemical manufacture, of which roughly 30% is based on petroleum hydrocarbons. These halogenated products include insecticides, fungicides, fumigants, weed killers, growth hormones, germicides, anaesthetics, refrigerants, anti-freezes, rubbers, paints, plastics, solvents, gasoline and lubricant additives and many others.

DDT, for instance, made from ethylene and chlorine, currently is being produced at the rate of 2,000,000 lbs. per month. Production of the weed-killer 2,4-D was 4,000,000 lbs. in 1947 and manufacturers expect this to climb to 100,000,000 lbs. annually. Both can be synthesized from petroleum hydrocarbons and chlorine. Enormous quantities of the Freons—fluorocarbons—are used as refrigerants while commercial applications for other fluorinated hydrocarbons are growing.

"Progress in Chlorination" was traced by E. T. McBee, Purdue University, from early inception to date in a review of the art in which much of his time has been devoted. He pointed out that the chlorination reaction is inhibited by oxygen; the rate is proportional to hydrocarbon and chlorine ratios in absence of oxygen; proportional to the square of the chlorine concentration where oxygen is present and inversely proportional to the concentration of oxygen, and the reaction is similar to that between chlorine and hydrogen. A number of useful correlations on rates of chlorination were presented, based on the chlorination of paraffins. He also brought out that chlorination of olefins is promoted by small amounts of oxygen and the reactions with other types of organic compounds also are treated. An extensive bibliography is cited.

Aliphatic Chlorination

"Directive Effects in Aliphatic Chlorination," by H. C. Brown, Purdue University, and A. B. Ash, Wyandotte Chemical Corp., reported the effects of substituents on the introduction of chlorine into aliphatic hydrocarbons, on which extensive information is unavailable. A quantitative study of the peroxide catalyzed chlorination with sulfuryl chloride was made with 1-chlorobutane, 1,1-dichlorobutane, 1,1,1-trichlorobutane, n-butyryl chloride and n-propyl acetate.

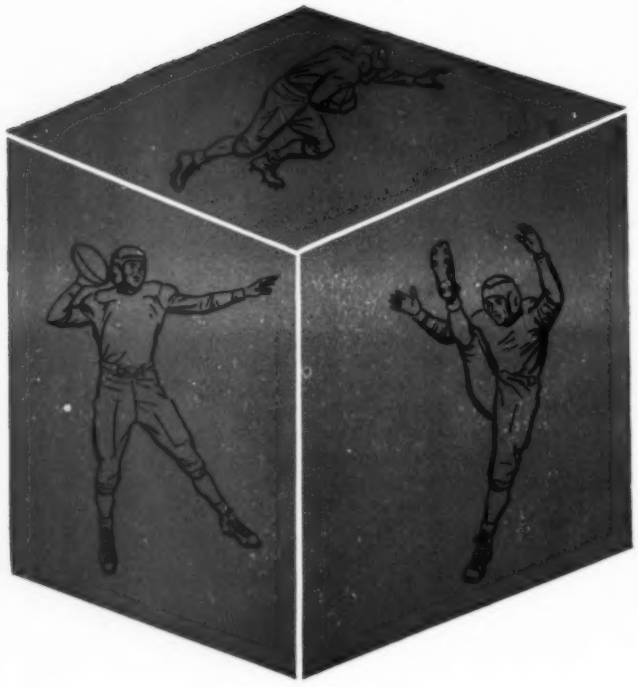
Presenting data in terms of the percentage of the various isomers recovered in the reaction mixture, the results include the following for the three chlorobutanes:

C — C — C — C — X				
24	47	22	7	Cl
37	49	12	2	Cl_2
51	49	0	—	Cl_3

and for the n-butyryl chloride and n-propyl acetate:

C — C — C — X			
48	49	3	COCl
29	46	25	O_2CCH_3

The effect of nine substituents in a linear three-carbon system toward further substitution by chlorine are given by similar data in the order of their decreasing activating effect: phenyl > CH_3 > H > O_2CCH_3 > CH_2Cl > $CHCl_2$ > $SiCl_3$ > CO_2H > COCl > CCl_3 > CF_3. The phenyl and methyl groups appear to be activating relative to hydrogen and direct substitution toward the carbon atom to which they are attached. The groups below hydrogen, however, appear to deactivate the carbon atom to which they are attached and direct further



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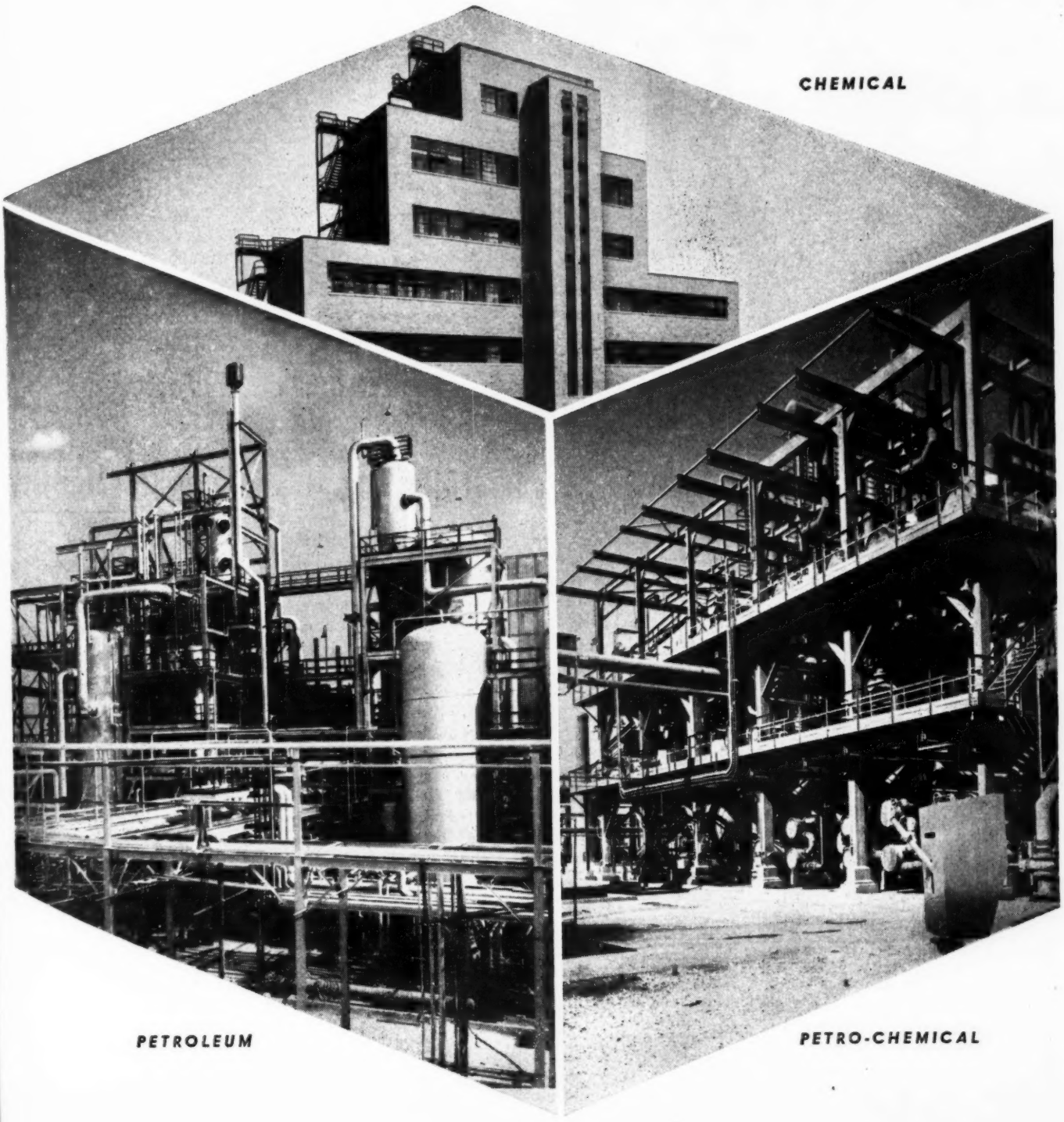

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substitution to more remote positions in the molecule.

Fluorination

There were several papers dealing with the fluorination of hydrocarbons, which, except for the Freons, constitute relatively new commercial products. B. H. Wojcik, Hooker Electrochemical Co., discussing "The Chemistry of Organic Fluorine Compounds," said that only during the war, with the investigations instigated during the development of atomic energy, did elemental fluorine become a commercial material; previously the production of hydrogen fluoride had made possible the Freons, and before that some organic fluorides had been prepared following the isolation of the element.

Currently, he stated, there are six methods by which fluorine can be incorporated into an organic molecule: By addition of HF to unsaturates, interaction of organic halides with inorganic fluorides, decomposition of diazonium compounds, by use of fluorine "carriers," fluorination with halogen fluorides, and direct fluorination with the element. It is believed that alkylation of petroleum hydrocarbons using HF as catalyst actually may involve the for-

TABLE 2—Processing Gasoline from Crude Petroleum

Primary Crude Distillation	Yield, Vol. % of Crude
C_3-and-Lighter and Loss	1
C_4-400° F. Gasoline	25
Kerosene Stock	12
Gas Oil	37
Lube Stock	7
Residuum	18
	100

Cumulative Processing Sequence for Increasing Gasoline Yield and Quality

Step No.	Operations	C_4-400° F. Gasoline Yield, Vol. % of Crude	Research Oct. No.	ASTM Motor Oct. No.
1	C_4-400° F. Virgin Naphtha from Crude	25.0	55	53
2	Add Thermal Cracking of:			
	(a) Gas Oil	15.0	70	63
	(b) Residuum	2.7	67	60
	Cumulative Total	42.7	61	57
3	Replace Thermal Cracking of Gas Oil with Catalytic Cracking	16.9	93	79
	Cumulative Total	44.6	70	63
4	Add Thermal Reforming of 200°-400° F. Virgin Naphtha	11.7	80	70
	Cumulative Total	39.1	83	73
5	Replace Thermal Reforming of 200°-400° F. Virgin Naphtha with Hydroforming	15.0	82	73
	Cumulative Total	42.4	84	74
6	Add Nonselective Polymerization of Butylenes and Propylene	2.4	98	83
	Cumulative Total	42.2	84.5	74.3
7	Replace Nonselective Polymerization of Butylenes and Propylene with Alkylation of Butylenes, Pentylenes, and Propylene	7.6	92	91
	Cumulative Total	42.8	85	76
8	Remove by Superfractionation of Virgin Naphtha: Normal Pentane, Normal Hexane, and Normal Heptane Cuts	(4.8)	52	51
	Cumulative Total	37.0	89	80
9	Add Isomerization of:			
	(a) Normal Pentane (To Ultimate Yield)	1.4	88	87
	(b) Normal Hexane (Once-through)	2.2	81	80
	Cumulative Total	40.6	89	80
10	Remove Raffinate Obtained by SO_2 Extraction of Hydroformates	(3.5)	35	34
	Cumulative Total	37.1	94	84
11	Add Thermal Reforming of Above Raffinate and n-C_7 Cut from Virgin Naphtha	2.7	74	64
	Cumulative Total	39.8	92.5	83
12	Add Vacuum Flashing and Deasphalting of Residuum to Obtain 14% Additional Heavy Gas Oil from Crude for Catalytic Cracking. Catalytic Cracking of This Gas Oil Produces Additional Naphtha and Additional Light Ends for Alkylation. Cumulative Gasoline Pool Becomes:			
	C_6-400° F. Naphtha from Catalytic Cracking	22.4	92	78
	Alkylate (Total Butylenes, Pentylenes, Propylene)	11.6	92	91
	Superfractionation and Isomerization Products:			
	Isopentane	3.6	88	88
	Isohexanes	3.6	81	80
	Isoheptane Fraction	3.1	72	71
	Extracted Hydroformates:			
	Toluene	1.8	120	110
	Xylenes	3.5	140	120
	Heavy Aromatics	2.9	100	80
	Thermally Reformed Raffinate (Includes n-C_7 Fraction from Virgin Naphtha)	2.7	74	64
	Subtotal	54.7	94	84
	Add Extraneous Normal Butane for 10 Lb. R.V.P.	6.0	95	95
	Total Gasoline Pool	60.7	94	85
13	Withdraw for 100/130 Grade Aviation Gasoline:			
	Butylene Alkylate	4.4	94	94
	Isohexane-Isoheptane Naphtha Fractions	6.6	76	75
	Isopentane Fraction	2.0	88	88
	Total 100/130 Aviation Gasoline (With 4 cc. TEL/Gal.)	13.0	85	84
	Remaining Motor Gasoline Pool	47.7		
	Back out Extraneous Normal Butane for 10-Lb. R.V.P.	0.8	95	95
	Final Motor Gasoline Pool with 1 cc. TEL/Gal.	46.9	97	85
			100	88

mation of an intermediate HF addition product. Various reactions producing fluorides by these six methods are discussed.

Characteristically, many organic fluorides are quite stable to heat and chemically inert. These properties are shown to increase as more fluorine is added to the molecule. As fluorine is added, the freezing and boiling points increase, but when substitution is complete, as in the fluorcarbons, boiling and freezing points are nearly the same as for the parent hydrocarbon.

Organic fluorides may be either toxic or non-toxic. From spotty available information, the indications are that fluorine compounds tending to eliminate HF are capable of releasing it on hydrolysis, or produce an anion containing fluorine during hydrolysis and oxidation, and are toxic. Compounds having more than one fluorine atom attached to each carbon atom generally are non-toxic.

Principal commercial products derived from fluorination of hydrocarbons include, besides the Freons, polymerized tetrafluoromethane as a plastic (du Pont's "Teflon") used in wire coatings and special gaskets, aromatic fluorides in the preparation of light and heat stable dyes, fluorolubes made by polymerizing perfluorovinyl chloride (outstanding as a lubricant for oxygen compressors and pumps handling peroxide solutions), and sodium fluoroacetate as a rodenticide. "Gix," 1,1-bis (fluorophenyl) trichloroethane, was used by the Germans as a more powerful insecticide than DDT.

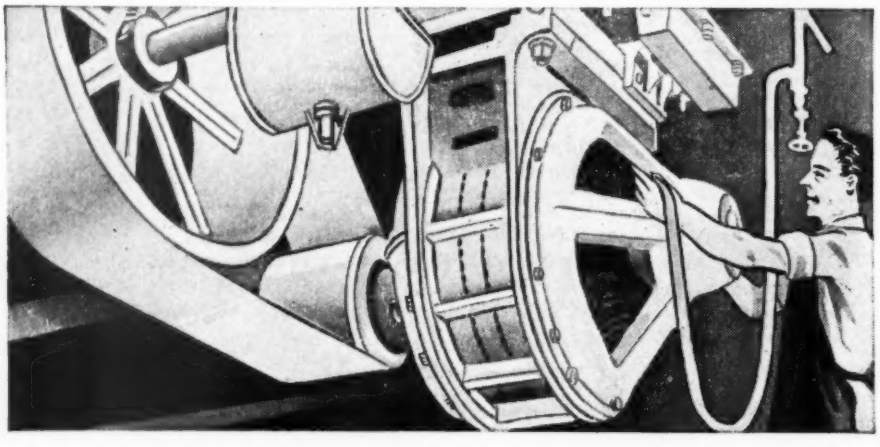
Another paper, "The Synthesis of Fluorocarbons," by R. D. Fowler, Johns Hopkins University, and C. E. Weber, General Electric Co., described several methods for the production of this class of fluorinated hydrocarbons. It was brought out that the Navy was particularly interested in them as possible non-explosive, non-inflammable liquids for recoil mechanisms of guns and the National Defense Research Council, Section S-1 (precursor of the "Manhattan Project"), was considering them as possible sealants, coolants and lubricants in handling of certain corrosive materials involved in the separation of uranium isotopes. Fluorocarbons of particular interest were those boiling around 212° F. and a group falling in the class of light oils. Full-scale commercial syntheses were the result of this work.

Another paper of interest dealt with the "Chemistry, Properties and Uses of Chlorinated Rubber and Chlorinated Paraffin," presented by D. R. Wiggam, W. T. Kiessling and J. B. Martin, Hercules Powder Co. In describing these materials, it was brought out that the first use of chlorinated paraffin was in pour point depressants and other oil additives in the early 1930's, and of chlorinated rubber as a film-former in paints; both subsequently were extensively used as flame-proofing materials.

Chlorinated paraffin is supplied as a viscous liquid or hard brittle solid, readily dissolved in numerous solvents and non-inflammable. Its principal uses are as a constituent in flame-proof paints and in flame-proofing textiles and the like, and in cutting and drying oils. Both applications make use of its property of releasing hydrogen chloride at high temperatures and relative stability at "normal" temperatures. Chlorinated paraffin also is used as a drying oil substitute and as an extender in alkyd resin paints.

Chlorinated rubber is a colorless, odorless white granular powder, soluble in numerous commercial solvents. It is extremely resistant to attack by acid or alkali and therefore has been widely used as a base for acid and alkali resistant paints, especially the concrete paints and those used for maintenance purposes in corrosive atmospheres. It also is used as a drying agent in rotogravure and lithographing inks, and as a base for soap-wrapper inks. Recent experimental work indicates that chlorinated natural and acrylonitrile-butadiene rubber combinations can be used to form clear films of high tensile strength, which show promise of being accepted as food wrappers. They are also used with alkyd resins in metal finishes to impart chemical resistance and speed up drying.

Other papers included in the symposium were "Preparation of Allylic Chlorides," by G. W. Hearne and T. W. Evans, Shell Development Co.; "Halogenated Hydrocarbons as Biocides," by R. Hansberry and S. C. Dorman, Agricultural Laboratory, Shell Oil Co., Inc.; "Hydrates of Halogenated Hydrocarbons," by F. Blankenship, J. E. Sampson and K. Williamson, University of Oklahoma. A fully automatic process for the synthesis of hydrogen chloride gas from cell chlorine and hydrogen, which delivers the anhydrous HCl to process at 20 psi. without use of compressors and blowers also was included because of its general relationship to the other papers and since it is useful in recovering by-product HCl resulting from organic chlorinations.



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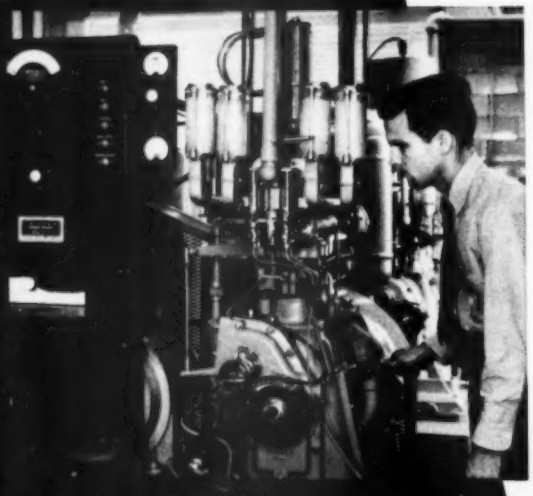
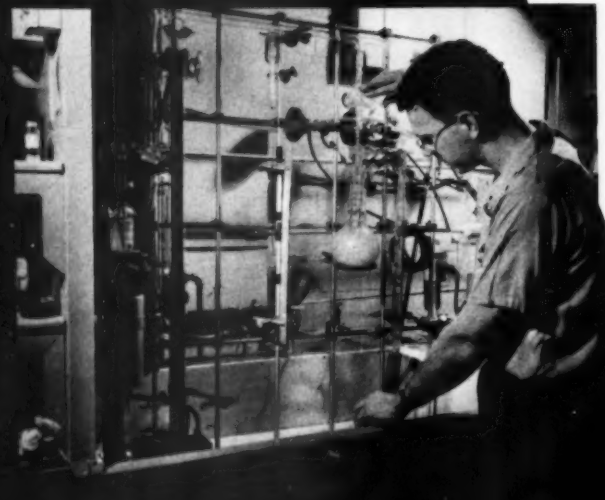


Apparatus in use by the Jackson Laboratory for studying rates of sublimation in connection with cylinder deposit studies.



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JACKSON LABORATORY—In this, the research laboratory of the Organic Chemicals Department, are developed new chemical compounds for use as fuel and lubricant additives.

PETROLEUM CHEMICALS LABORATORY—Work is done here on development and application of petroleum additives other than antiknock agents.

OTHER RESEARCH GROUPS—Close liaison is continually maintained with other Du Pont research groups for any possible development that may have application in the improvement of petroleum products.

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Toxic Properties of Refining Chemicals Listed by API Medical Committee

THE toxicology of 11 chemicals handled in volumes in modern refining, and of three aromatic compounds synthesized from petroleum, is presented in a series of reports prepared under the supervision of the Medical Advisory Committee of the Department of Safety of the American Petroleum Institute.

Some 25 to 30 more substances are to be reported on as part of the present project. Thus, eventually, there will be available to refiners complete data to aid them in their precautionary measures to prevent the exposure of workers to any of the large number of chemicals used in modern refining. The reports were prepared by the Harvard School of Public Health, under the direction of Prof. Philip Drinker, who is a leading authority on industrial hygiene.

Aiding in their preparation are the 20 members of the API Medical Advisory Committee, all oil company staff physicians, and 21 associate members of the committee, largely oil company technologists who have worked on the development of the modern refining processes in which the chemicals reviewed are employed.

The API Medical Advisory Committee was set up in 1945 to undertake this work. It was recognized that the evolution of petroleum refining from a relatively simple process of thermal distillation and acid treatment of products to a variety of complex catalytic cracking and numerous other involved processes and treatments brought about a need for accurate and concise information on the toxic properties of substances handled and used in the plants today.

It is generally recognized, states the foreword of the general review, that in most instances the materials encountered in the petroleum industry do no harm to those who contact them. A few are capable, however, of producing toxic effects and may cause local or systemic injury in cases where a sufficient quantity of a toxic agent remains in external or internal contact with the body for a sufficient quantity of time. The term "sufficient quantity" and "sufficient time" will vary widely, it is pointed out, depending on the inherent toxicity of the individual substance involved and the susceptibility of the individual.

"Inasmuch as contact with most petroleum products does no harm," the review continues, "most individuals give little thought to the possibility of poisoning due to inhalation or skin contact with any such substances, especially as they are unaware that the skin may fail to exclude the toxic agent, or that considerable amounts may be absorbed from the air they breathe.

"Poisoning occurring as a result of skin contact, or inhalation, may develop insidiously over a long period of time; and, as local irritation of the skin or respiratory tract may be entirely absent, the relationship between exposure and effect may be completely overlooked. Prevention of such delayed or insidious poisoning depends on familiarity with the possible toxic effects of the various agents encountered, as well as constant vigilance to keep such contact at a safe level. It is hoped the API toxicological reviews will serve such a function."

The toxic substances studied, for convenience and simplicity, were divided into the following classifications:

1—Irritants: This class of gases, mists, vapors and dusts injures the air passages or lungs and induces inflammation of the respiratory tract. These local effects overshadow any systemic effects occurring following absorption. Examples are ammonia and acid gases or mists, such as sulfur dioxide or sulfuric acid mists.

2—Asphyxiants: This group of substances acts by virtue of the exclusion of oxygen from the tissues. Two groups of asphyxiants are recognized. The simple asphyxiants such as methane, hydrogen or nitrogen, when breathed in sufficient concentration, mechanically exclude oxygen from the lungs. The chemical asphyxiants such as carbon monoxide, hydrogen sulfide or hydrogen cyanide interfere with oxygen transport by the blood, or oxygen utilization by the tissues.

3—Volatile Drugs and Druglike Substances: "This group contains substances which do not injure the air passages or lungs," states the review, "but act after absorption by the blood and transportation to the tissues of the body. A large group of volatile hydrocarbon substances are included in this group. It is divided into various sub-groups, depending on the type and duration of disability or injury produced by the substance.

"It is not possible to predict accurately what sub-group a particular hydrocarbon or related molecule will occupy, but the following general rules are helpful:

"The unsubstituted aliphatic hydrocarbons usually exert an anesthetic or irritating effect on the nervous system but seldom produce lasting injury. Aromatic hydrocarbons, on the other hand, are prone to produce lasting damage to the body, especially to the blood-forming tissues. Chlorine-containing hydrocarbons typically exert a deleterious effect on the liver. Sulfur- or nitrogen-containing hydrocarbons may have varied severe and unpredictable systemic toxic effects."

4—Inorganic and Organometallic Substances: This group contains a variety of substances of interest to the petroleum industry, such as inorganic phosphorus compounds or substances such as tetraethyl lead or iron carbonyl. As the toxic effects of the various substances encountered in the petroleum industry vary widely, it is not possible to generalize the question of treatment.

The information in the individual toxicological reviews includes the following, among other data: Identification of the substance and its general physical and chemical properties, emphasizing the characteristics influencing volatility, as these influence the degree of atmospheric exposure which is likely; probable con-

How to Buy the Reports

The API Toxicological Reviews are published in the form of individual bulletins for each toxic substance reviewed, of four to eight pages, in form for collection in standard ring binders. The 14 reviews so far issued are available at 25c each, with discounts for quantities when shipped to a single address. A standard ring binder appropriately stamped can also be purchased. Address Department of Safety, American Petroleum Institute, 50 W. 50th St., New York 20.

TABLE 1—Characteristics of Toxic Chemicals Used in Petroleum Refining or Synthesized from Petroleum

Substance	Use in Processing	Maximum Safe Concentration 8-Hr. Period	Principal Source of Exposure
Aluminum Chloride $AlCl_3$	Isomerization and condensation catalyst	10 ppm	Skin or eye contamination through splashing when compound comes in contact with moisture.
Boron Trifluoride BF_3	Manufacture of polybutylene and other materials	3 ppm	Direct contact and inhalation through failure of containers or pipelines. Adequate ventilation will prevent exposure to low concentrations in open rooms.
B,B' Dichloroethyl Ether (Chlorex) $(CH_2Cl \cdot CH_2)_2O$	Solvent refining of lubricating oils	15 ppm	Inhalation of vapors from leaks in closed system, or skin contact with liquid when repairing or refilling unit.
Cresol $C_6H_4(CH_3)OH$	Solvent refining of lube oils and as additives for lube oils		Skin contamination following breaks in equipment or when adding material to closed systems.
Cumene $C_6H_5CH(CH_3)_2$	High octane blending component	50 ppm	Direct skin contamination. Amounts present in gasoline too low to be of toxicological significance
Furfural $C_4H_3O \cdot CHO$	Solvent refining of lube oils and separation of butadiene from other compounds		Skin contamination, appreciable vapor concentrations unlikely.
Hydrogen Chloride HCL	Used in isomerization process, purification of filter clays, by-product in gasoline sweetening	10 ppm	Skin contact and inhalation following escape of HCl gas from leaks or breaks in equipment.
Hydrogen Sulfide H_2S	Contaminant encountered in handling and refining high-sulfur crudes	20 ppm	Inhalation and skin contact with the gas in working areas.
Iron Carbonyl $Fe(CO)_5$	In laboratory and in preparation of catalysts for hydrocarbon synthesis	100 ppm	Exposure, usually to vapor following leaks or spills.
Nitrobenzene $C_6H_5NO_2$	Solvent refining of lube oils	5 ppm	Skin contact with liquid or vapor when breaks or leaks occur in closed systems. Laboratory work may present risk of exposure.
Styrene $C_6H_5CH{=}CH_2$	In production of synthetic rubber and as starting point in manufacture of emulsifying agents for oils and distillation	400 ppm	Contact with vapors or liquid as result of leaks or spillage of material
Sulfuric acid H_2SO_4	Extensively used in petroleum refining		Skin contact with liquid acid and, less frequently, skin and respiratory tract contact with vapors through leaking of acid lines, etc.
Toluene $C_6H_5(CH_3)$	Synthesized from petroleum	200 ppm	Skin contamination following spillages and breaks in processing system. Exposure to vapors in laboratory.
Xylene $C_6H_4(CH_3)_2$	Synthesized from petroleum	200 ppm	Skin contamination where spillage, leaks or breaks occur.

ditions and sources of exposure; toxicology of the substance including safe limits of exposure for an 8-hour period 5 days a week; treatment of poisoning; precautionary measures in handling the substance; determination of concentration in atmosphere; selected bibliography. Accompanying Table 1 lists the toxic substances included in the present reports with a few characteristics. Below is an abstract of selected information from the individual reports.

Aluminum Chloride

This substance fumes in moist air, being readily hydrolized to $Al(OH)_3$ and HCl in the presence of moisture. Under certain conditions the reaction between moisture and $AlCl_3$ may not take place at once, but HCl may be liberated on standing. If the surface of a mass of anhydrous $AlCl_3$ is allowed to "glaze" with a coating of $AlCl_3 \cdot 6H_2O$ and the mass is then sealed in a tight container, the H_2O of the hydrate slowly diffuses to the remaining anhydrous material and reacts to form aluminum oxide and HCl gas.

As the reaction proceeds, the pressure of the HCl gas becomes strong enough to burst the container. A glass bottle filled with $AlCl_3$ which has been exposed to the open air for a few minutes before being placed in the bottle may blow its stopper in this way. Large drums filled with the commercial product have been known to explode, probably from this cause.

Aluminum chloride must be handled so that it has the least possible contact with moisture or moist air. It should be stored in airtight sheet-iron drums. Any HCl formed as a result of contact with moisture will result in corrosion of containers. When $AlCl_3$ is used in technical operations it should be transferred from one container or vessel to another in a totally enclosed line, duct or screw conveyor. HCl evolved as a result of the reaction of $AlCl_3$ should be removed and trapped out in water, rather than released into the air.

Boron Trifluoride

Very soluble in water, alcohol and ether, Water at ordinary temperatures will absorb about 700 times its volume of BF_3, forming a syrupy liquid. Absorption proceeds rapidly with the evolution of heat, so that sucking back must be controlled in any system in which gas is introduced under the surface of the liquid. In water BF_3 forms hydrofluoboric acid (HBF_4). Concentrated solutions attack glass, but dilute do not. This acid will combine with various bases to form a series of well defined salts, the fluoborates.

B,B' Dichloroethyl Ether (Chlorex)

It is stable, does not corrode iron and possesses the solvent properties of ethyl ether and ethylene dichloride. It is insoluble in water but is soluble in most organic solvents. Chlorex dissolves many tars, waxes, oils, resins and gums. It will dissolve ethyl cellulose, but does not dissolve cellulose except in conjunction with 10 to 30% alcohol.

No special safety measures are nec-

essary for workers other than sufficient ventilation to keep the vapor concentration below 15 ppm. The odor and irritant qualities of this solvent provide adequate warning of the presence of excessive concentrations.

Cresol

No limits for cresol vapor in air have been established, as no cases of poisoning due to inhalation have been reported. Danger of poisoning appears to be limited to actual contact with the liquid. Processes should be as completely enclosed as possible to prevent splashing. Special precautions should include:

"Gage glasses on apparatus containing cresylic acid or cresol should be protected with a cover glass, and the column equipped with a ball check valve to prevent spillage in the event the gage glass breaks.

"Men unavoidably encountering severe exposures should be protected by synthetic rubber protective equipment consisting of gloves, cover-all type suit, hood for head and shoulders, boots and acid-proof goggles. Ordinary production workers should be required to use gloves, apron, well-fitted cap-type goggles, face shield and boots.

"Tanks which have contained cresol should be cleaned with dilute caustic and live steam prior to being entered for repairs, and forced ventilation or an air hose mask should be required.

"Containers should be labeled properly and inspected frequently for evidences of corrosion or leaks."

Cumene

During the war cumene was used in considerable quantities as a high-octane blending component for aviation gasoline. Its production is now drastically curtailed, although it is still encountered in laboratory operations. Contact is limited essentially to skin contamination of workers and maintenance personnel within refineries. Inhalation contact is limited by the low volatility of cumene. The amounts present in gasoline are too slight to be of toxicological significance.

Furfural

Formed from bran by condensation of pentoses in the presence of dilute sulfuric acid. Furfural finds extensive use for the solvent refining of lubricating oils, resin and other organic materials; also used in the separation of butadiene from other compounds in the production of synthetic rubber. Contact is primarily limited to skin contamination; appreciable vapor concentrations are unlikely. As a result of being relatively non-volatile, it has been used in industry for 20 years without any definite evidence of toxicity being encountered.

Hydrogen Chloride

Anhydrous hydrogen chloride was extensively used during the war as the reactive constituent of the catalyst used in the isomerization process, where skin contact and inhalation was a possible source of exposure following breaks in equipment. Minor degrees of contact are possible from the use of hydrochloric acid as a purification agent for filter clays and from its formation as a byproduct when copper chloride is used in sweetening gasoline.

Precautionary measures include proper ventilation and mechanical safeguards to prevent inhalation and skin contact with HCl vapor or solutions. If large amounts of the material must be handled, respirators, goggles, and rubberized gloves, aprons and boots should be provided. Sudden high concentrations of anhydrous HCl in the air should be capable of temporary control by directing a stream or spray of water at the area, as the water will dissolve the HCl.

Hydrogen Sulfide

Oil companies have had much experience with this substance in the production, transportation and refining of high-sulfur crudes. Highly toxic concentrations of H_2S may be encountered in the air above crude oil or distillates contained in tankers or storage tanks. Concentrations as high as 1% have been observed. The vapors present in or coming from crude stills are especially high in H_2S. Fortunately, H_2S is gradually eliminated in the refining processes and is virtually absent in the finished product.

Some petroleum additives contain sulfur compounds which, if heated, may break down and release hydrogen sulfide, the concentrations possibly reaching dangerous levels if the heating process takes place in a closed or semi-closed vessel. Hydrogen sulfide may be absorbed in water or sludge in crude oil storage tanks, and may be released by agitation or by the sun's heat during cleaning operations and thereby present a hazard to workmen.

Iron Carbonyl

While this is a highly toxic substance, its use in this country is limited to laboratory operations and the preparation of certain catalysts for hydrocarbon synthesis. Exposure is usually to the vapor, following leaks or spills. Laboratory operations involving the use of the carbonyls should be carried on in well ventilated hoods. If exposure is unavoidable during the repair of equipment, an approved type fresh-air hose mask should be worn and skin contact prevented by the use of rubberized gloves.

Nitrobenzene

Nitrobenzene is employed in the solvent extraction of lubricating oils, in closed systems, and exposure to liquid or vapor will come when breaks or leaks occur and when additional material is added to the system. Laboratory work may present greater risk of exposure.

All possible operations should be mechanized and carried out in a closed system to reduce chance of exposure to the minimum. Ventilation should be sufficient to prevent accumulation of nitrobenzene vapors in excess of 5 ppm.

Styrene

Styrene is a moderate eye and respiratory irritant. Although inhibitors must be added to styrene to prevent spontaneous polymerization, the quantities added are too small to be toxicologically important. In addition to being used extensively in the production of synthetic rubber and

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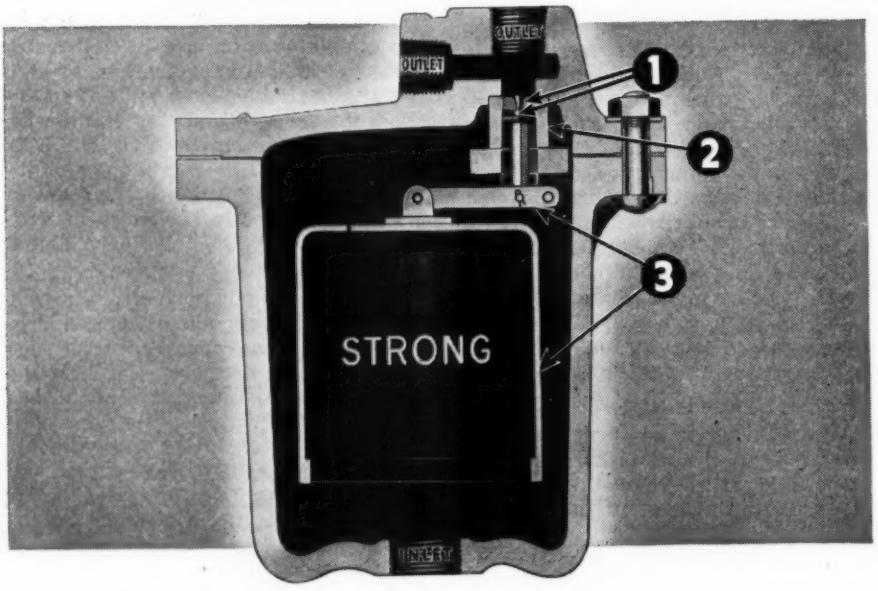

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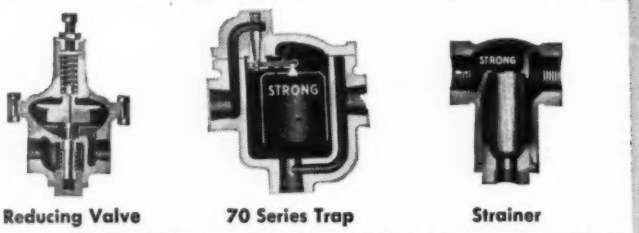

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resins, it is used in the petroleum industry as a starting point in the manufacture of emulsifying agents for distillates and oils. Respiratory equipment should be provided for all workers who must undergo exposure to concentrations in excess of 400 ppm.

Sulfuric Acid

The handling of this chemical in large quantities in refineries has developed to a point where accidents are usually the result of failure to follow established working rules. In addition to wearing the proper clothing, workers subject to exposure should be educated concerning the dangers of sulfuric acid, as well as concerning proper emergency measures, and the location and proper use of emergency equipment. Key personnel should be drilled in the use of emergency equipment and the handling of acid burns. Equipment should be inspected and serviced regularly.

Areas where sulfuric acid is used should be so constructed that slipping or tripping will not occur. Sulfuric acid pipelines should be located above ground for safety, as leaks will be more apparent and inspection easier. Lines which must be dismantled should be locked closed on each side of the break and then drained. Lights and fires should be kept away from H_2SO_4 lines or storage tanks, as hydrogen may be evolved from the action of the acid on certain metals.

Toluene

Where synthetic toluene is produced from petroleum, skin contamination may result from spillages, leaks or breaks in the processing system. Some hazardous exposure to toluene vapors may be encountered, particularly among laboratory workers who use it as a solvent or reagent. General ventilation should be adequate and should be supplemented by local exhausts wherever excessive concentrations are to be expected. Air tests should be made at regular intervals to insure maintenance of a concentration below the accepted safe limit of 200 ppm for exposures not exceeding a total of 8 hours daily.

Xylene

Contact with xylene is not great as it is relatively non-volatile. Laboratory workers may contact excessive vapor concentrations, whereas skin contamination among refinery workers usually results from spillages, leaks and breaks. In petroleum refining, xylene is encountered principally in the heavy ends of gasoline or naphthas obtained from thermal or catalytic cracking and from polyforming and hydroforming operations. Although less volatile and less toxic than toluene, good general ventilation, supplemented by local exhausts where concentrations may be excessive, is essential.

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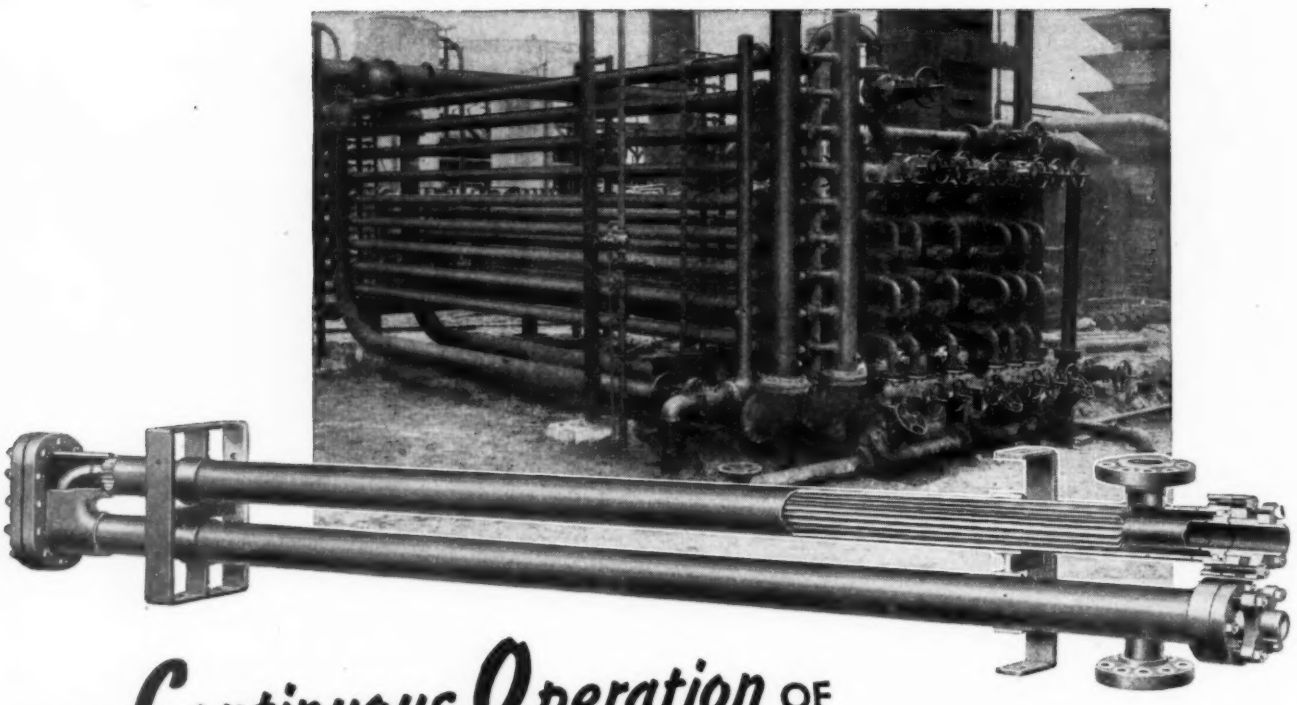

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Gasoline and Cycling Plant Operation

Conducted by DAVE THORNTON

Data in answer to questions presented on these pages is supplied through the cooperation of authorities with the equipment and engineering companies of the Natural Gasoline Supply Mens Assn., among others. Readers are invited to submit queries on plant operating problems in their own work.

Do unitization programs tend to squeeze out the independent operator?

I wish I could solve the problem of what happens to "squeeze out" the independent operator. It looks more and more like many are being "squeezed *into*" the business. I don't think you can say that because we are going through a change in the complexion of the production of oil and gas, people are being squeezed out of the business.

It seems to me there are opportunities now in unitization programs for the small investor to get an adequate return on his money. Also, of course, there are a few places where a unitized program goes in and necessarily the equities have to be readjusted.

Those people whose equities are readjusted upward are hurt because the proration schedules do not very often approach what engineers now claim to be the equities of the field. So we get into the argument of "Who is going to get what?". Whether a man is squeezed out depends on whether or not he is going to get more or less than he has made.

I don't believe you can blame the unitization program for "squeezing out" the independent operator. I think he has a greater opportunity today to participate in the efficient production methods and obtain the most recovery from the maximum product that can be made from the fields through a unit program because he could not afford to build a plant on his own particular lease. —J. R. Bulter, J. R. Bulter & Co., Consultants, Houston.

Please describe a recommended temperature control for maximum recovery of propane in the kettle product of a de-ethanizing fractionator, when feeding a raw material of variable composition.

Theoretically a change in feed composition should result in a change of tray to which the feed stock is admitted, hence maintaining the same material balance in the column. As the feed becomes richer in ethane the admission of the feed to the column should progress upward; conversely, as the feed becomes richer in the higher hydrocarbon the feed should be placed in the column at a lower level. The feed composition should be the same as the normal composition of the material on the tray to which it is admitted.

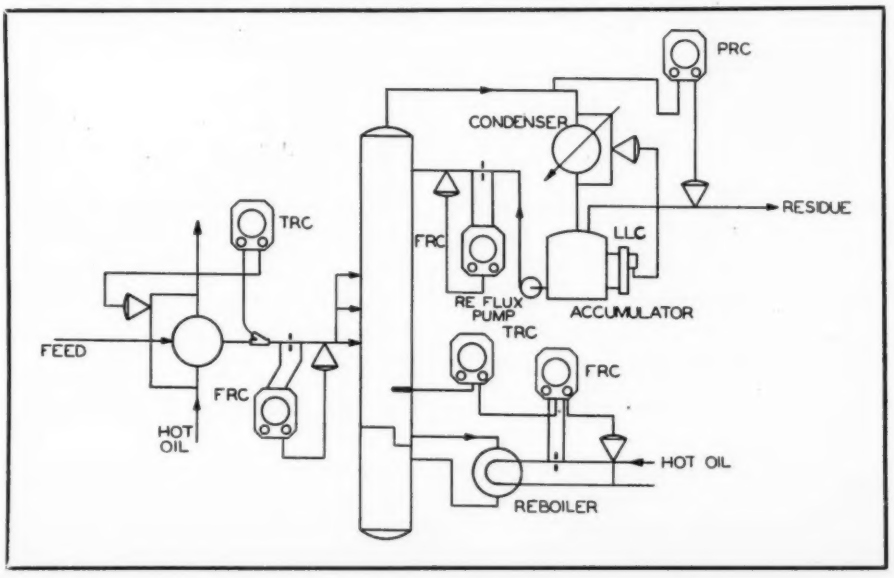
Since this means of control is not practical, I consider the next best thing would be to fix the reflux rate to the column, and adjust the heat input to the reboiler to maintain a constant tray temperature somewhere in the column. The selection of the proper tray for the temperature control should be such that a change in temperature is indicative of a material change of the composition of the hydrocarbons on that tray.

The instruments widely accepted for this control are a temperature controller with automatic reset, resetting the set point of a pressure controller if steam is used, or a flow-controller if hot lean oil is used for heating the reboiler.

Other instruments essential for this application would include flow and temperature control on the feed, level control on the bottom, flow control on the reflux, and pressure control on the column. The accompanying illustration is a schematic sketch of a proposed method of control.—G. E. Howard, Application Engineering Dept., Taylor Instrument Co., Rochester, N. Y.

What is the best source for high pressure vaporization equilibrium data?

There are three general types of problems which may require equilibrium data: (1) separators and fractionators at pressures of 300-1200 psi., (2) absorbers at 1800-2000 psi. and (3) reservoir fluids at pressures of 2500-8000 psi. It is assumed that "high pressure" refers to pressures above which the ideal equilibrium constants[1] should not be used. For a careful study of a specific problem, a literature study might show data on a mixture similar to that for which equilibrium data are desired.



De-ethanizer controls for maximum C_3 recovery as bottoms

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A bibliography[5] shows 45 articles dealing with complex mixtures.

For light hydrocarbons, the data of Roland Smith and Koneler[2] are good except that separations were not made between iso- and normal butane or pentane. It is necessary to cross plot the data as log K versus normal boiling point. The mixtures probably contained 25% of the butanes as iso-butane and 35% of the pentanes as iso-pentane. For absorbers, specific data were obtained by Webber[3]. However, the charts based on the crude oil-natural gas system (1) do not vary too much from that obtained with the absorber oil. To find the influence of the chemical nature of the absorber oil, Kirkbride and Bertelli[6] will be helpful. High pressure equilibrium constants for reservoir conditions are difficult to predict. After consulting the earlier data [1, 2, 9], the more recent article by Roland[4] shows the type of behavior which may be expected at pressures up to 9300 psi.

A general correlation of equilibrium constants is now in the manuscript stage for Section II of "Natural Gasoline and the Volatile Hydrocarbons"[8] and will present tables of constants using a series of convergence pressures to include constants for all types of hydrocarbon mixtures.—Donald L. Katz, Professor of Chemical Engineering, University of Michigan.

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(9) Standing and Katz, *A.I.M.E. Trans.*, 155, 232 (1944).

What are the possibilities of hypersorption as a process for increased propane recovery?

The recovery of propane from natural gas and refinery gas streams is a very useful application of the Hypersorption process. The operation readily effects essentially complete recovery of the propane from such gas streams. Dry gas effluent of a natural gasoline plant can normally be processed directly for complete propanes recovery.

The process employs a moving bed of activated carbon to absorb the hydrocarbons out of the lean gas stream and achieves pronounced selectivity in the adsorption of propane as well as other hydrocarbons. Details of the process were presented in a paper at the Houston meet-

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ing of the A.I.Ch.E. in 1946. Decriptions of the first operating commercial plant have been given in several recent papers, including one in the July issue of "Petroleum Processing." (See PETROLEUM PROCESSING, April, 1947, p. 300; July 1948, p. 635 —Ed.)

The extent to which Hypersorption extends the practical limit of recovery over the previous possibilities with oil absorption may be best illustrated by considering a typical absorber dry gas stream containing 8% propane. Here oil absorption recovery in new facilities would normally show minimum propane cost at 82.5% recovery; on the other hand, Hypersorption recovery costs show a minimum at 98% recovery. The recovery costs for propane by Hypersorption in this case would be, roughly, one-quarter of the optimum costs by the oil absorption method. In view of these lowered costs, recovery of propane from streams containing as low as 1.5% propane may be economical.

The first large Hypersorption unit for propane recovery is now being constructed and will have a capacity of 60,000,000 cu. ft. of gas per day. A similar large Hypersorption unit is also being constructed for recovery of both ethane-ethylene and propane-propylene from refinery gas. Rapid expansion of the number of units in these applications is expected.—Clyde Berg, Process Development Dept. Union Oil Co. of California, Los Angeles.

What is the best source of information for latent heats of gasoline hydrocarbons at elevated temperatures and pressures?

To the author's knowledge, there is no single source of information which tabulates all latent heats of vaporization for the hydrocarbon components of gasolines up to temperatures and pressures approaching the critical temperature and pressure of the components. The information is scattered in the literature, and data on the hexanes and heavier hydrocarbons are very meager.

If data on the vapor pressure, temperature, and volumes of the saturated liquid and vapor are known, the latent heats of vaporization at any temperature and pressure can be rigorously calculated by use of the Clapeyron equation.(6) A number of methods have been proposed for estimating the latent heats of vaporization at any temperature and pressure up to the critical, knowing only the critical temperature and the heat of vaporization at one temperature or the normal boiling point and the critical temperature.(10,15,16) These methods predict results with errors less than 5%. Several methods have been described for calculating the latent heats of vaporization of hydrocarbon mixtures such as gasolines and are discussed in an article on hydrocarbon thermodynamics by Edmister.(4)

Work under A.P.I. Project 44 by the Bureau of Standards tabulates latent heats of vaporization of hydrocarbons at two temperatures, 25° C. and the normal boiling point of the hydrocarbon.(13) These data are particularly useful as a starting point in the application of the correlations mentioned previously.

One of the most recent tabulations for the latent heats of methane and ethane is that of Hurd and coworkers.(1,9) Hanson, in 1946, tabulated the latent heats of vaporization of propylene, propane, isobutane, isobutylene and normal butane.(5)

Latent heats of pentane and isopentane have been reported by Sage, Evans and Lacey(14) and Beall.(2,3) Sidney Young, one of the early workers in this field, reports the heats of vaporization of normal hexane and 2, 3-dimethyl-butane from 0 to 235° C.(17) Lemons and Felsing(8) determined the latent heats of normal hexane, 2-methyl pentane and 2, 3-dimethyl butane from 0° C. to the normal boiling points. Pitzer(11,12) determined the heats of vaporization of normal heptane, 2, 2, 4-trimethyl pentane at their normal boiling points and that of 2, 3, 4-trimethyl pentane at 25° C.

Of interest is a report issued by the Bureau of Standards in 1935 which lists the experimentally determined heats of vaporization of eight gasolines, including a natural gasoline, and aviation gasoline, a straight-run naphtha and a cracked naphtha.(7)—F. H. Poettmann, Research Dept., Phillips Petroleum Co., Bartlesville.

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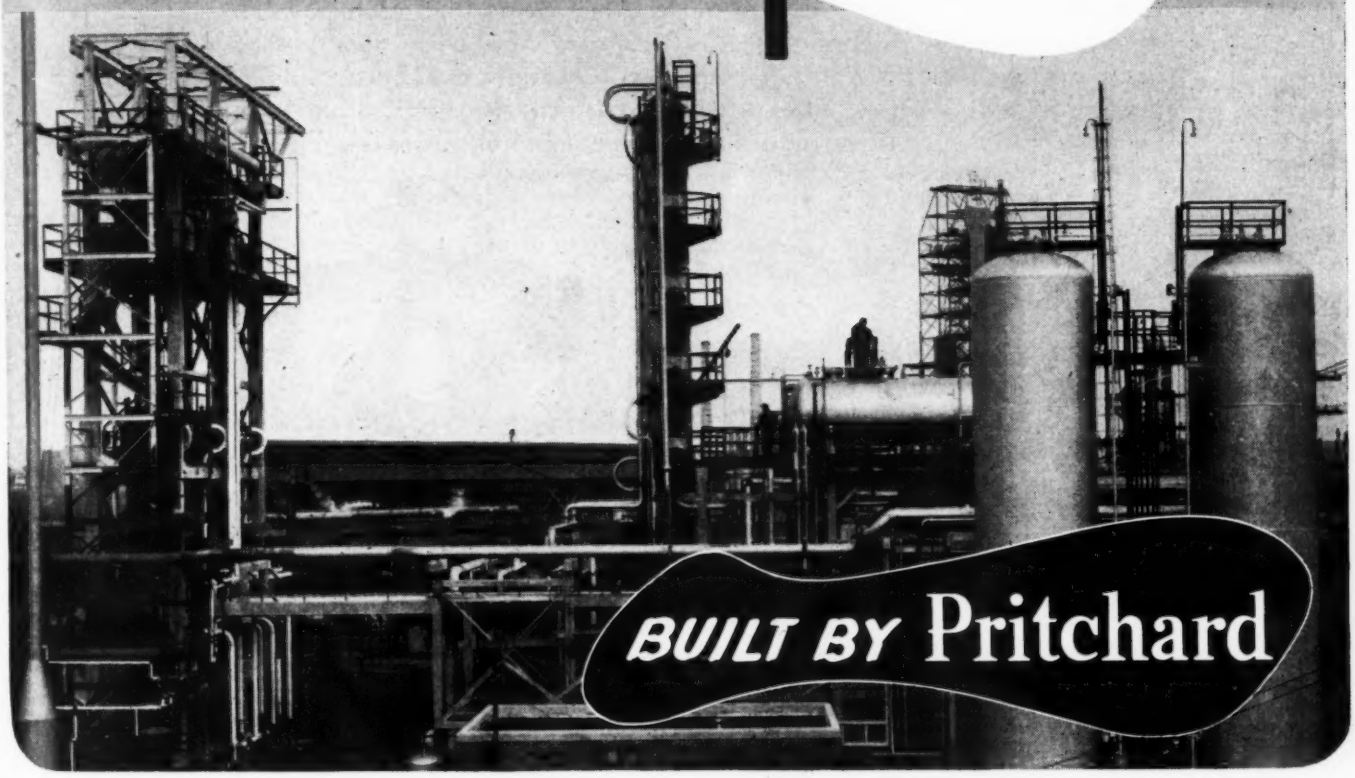

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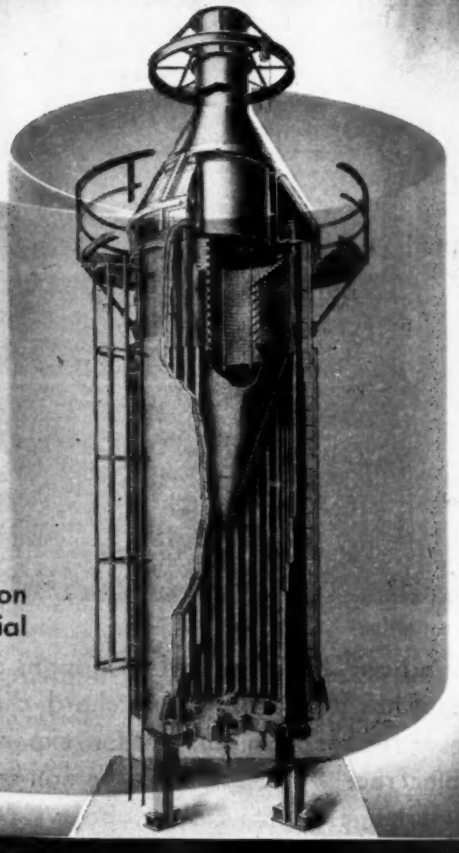

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BURN ACID SLUDGE UNDER BOILERS

While It Costs More to Prepare and Burn Sludge Than to Use Other Fuels, as a Means for Waste Disposal This Method Was Found Most Practical of Many Tried at a Texas City Refinery

By D. P. THORNTON, Jr., Assistant Editor

SULFURIC acid sludge is burned under boilers at Pan American Refining Corp.'s Texas City refinery to avoid the usual troubles in disposing of this common form of refinery waste. The plant operators do not claim it is the answer to all their difficulties with this material but it causes the fewest headaches of any of several disposal methods tried.

Features of this acid sludge disposal method are a homogenizing mill, between the circulating pump and sludge burners, which grinds the chunks of sludge into small particles, producing a relatively homogeneous mixture, and a governed rate of consumption under boilers which does not permit accumulation of any great amount of the material over any 24-hour period.

The sludge still is corrosive, eats holes in lines, and erodes burner tips; but plugging of lines, tanks and burner orifices, and accumulation of deposits on tubes and boiler settings have virtually been eliminated. Likewise, complaints of soot and acid fumes from a nearby residential section are very seldom received.

Approximately 100 bbls. of sludge are consumed daily. In addition to various unidentified chemical compounds and particles of carbon it contains up to 60 or 70% dilute sulfuric acid.

The story of acid-sludge disposal troubles at Pan American commences very nearly from the date the plant was first operated. Undoubtedly some of the experiences described below have been shared by many other refiners.

In the early days acid sludge, then as now, coming from treating of fuel oils with sulfuric acid, was run to the refinery sewer. Both Pan American and the pollution authorities were worried about contamination in Galveston Bay and the refinery began an investigation to determine what could be done to prevent possible contamination.

Filtration Unsuccessful

The most obvious solution was the use of filters to remove carbon particles which floated on the surface of the water and might have developed into a major basis of complaint. The acid content caused little objection, since it was sufficiently reduced by dilution with water and also could have been chemically neutralized if necessary.

Hay filters first were tried in the separator effluent ditch, but were not an outstanding success because they

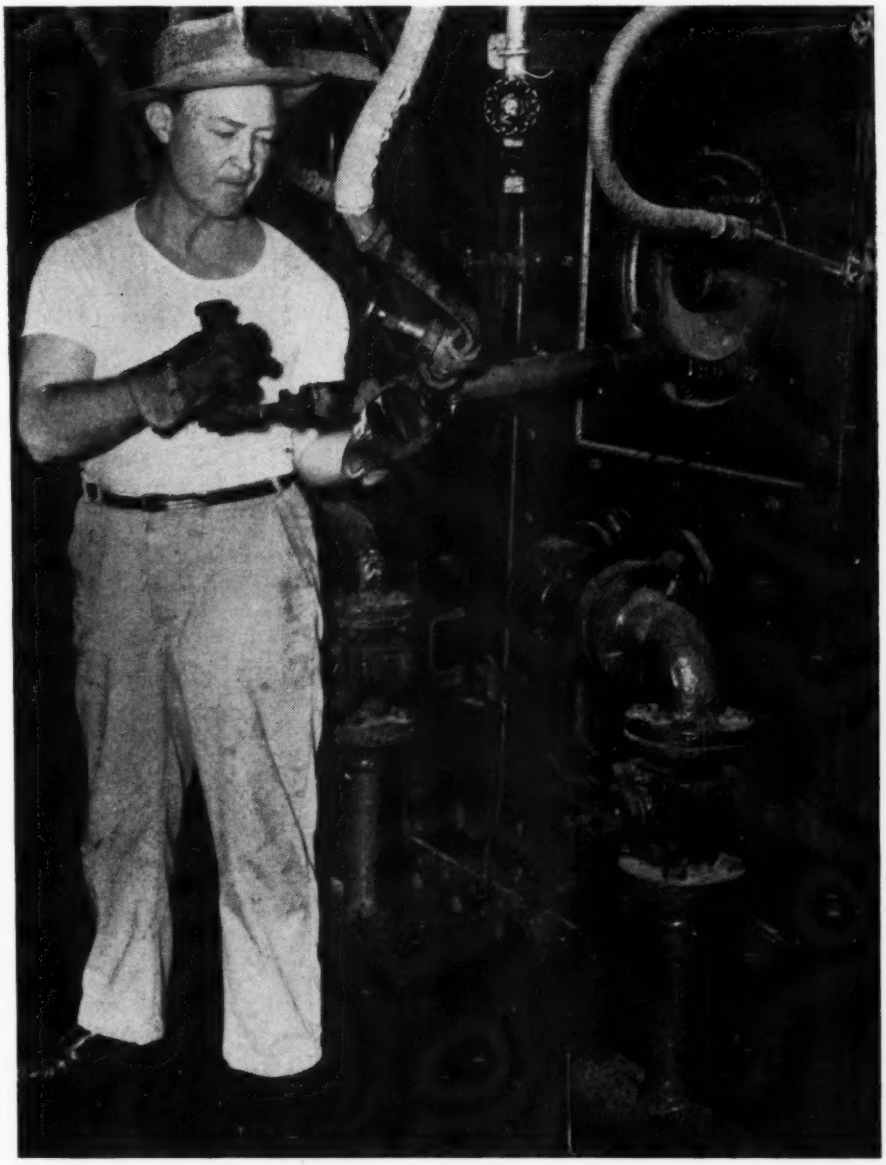

Fig. 1—Workman removing Pan American's home-made acid sludge gun from Peabody gas ring burner on boiler. Removal for maintenance, repair or replacement is possible without disturbing gas ring burner or air-flow setting

plugged readily and did not stop all of the sludge. Various types of baffling also were installed. The net result was that carbonaceous particles, carrying considerable adsorbed acid, continued to float through the system and into the Bay. Three possible solutions to the difficulty then were proposed:

1) Send to an acid recovery plant (in tank cars) at the outskirts of Houston, 40-odd miles away.
2) Burn in slop pits.
3) Burn under refinery boilers as an auxiliary fuel.

None of these proposals had any economic advantages. Indeed, the acid recovery plant would neither purchase the material nor return the recovered acid, but it would "accept" the sludge. Incidentally, this deal subsequently collapsed and not a car ever was shipped. Heating value of the sludge as a boiler fuel, it was believed, would not be sufficient to pay for the trouble and expense incurred in getting it to burn satisfactorily. This belief has proved accurate.

The second method, considered the least expensive in terms of equipment, was the first tried. The sludge was dumped in the pit and a gas flame directed against it. Little sludge was successfully burned. Much of it solidified to the extent that it had to be dug out of the pit and spread on waste-land nearby. It eventually was covered over by dirt hauled in for the purpose.

Considerable time and money were spent in developing several designs of a fire-brick retort, where it was intended to burn a pool of the sludge in a gas flame.

However, by the time a reasonably satisfactory design had been developed, the amount of sludge to be disposed of daily was triple the volume when refining operations first commenced, due to changes in plant operation. Sludge could be burned in the retort but neighbors complained of the objectionable soot and fumes. Thus development of some other disposal means was necessary.

The retort finally was replaced by another, in which sludge was burned inside a cone of gas flame. This was early in 1937. It then appeared that this method was satisfactory in that sludge was being burned and the neighbors were not complaining. However, so erratic was the composition of the material that a man had to be kept on duty 24 hours daily to adjust the flame and break up the crust of partially burned material. This continually built up in the bottom of the retort and on the walls, even ate holes through the retort several times.

Fig. 2—"Homogenizing" mill used to fluidize acid sludge before it goes to boilers or surge tank. This operation prevents solidification in surge tank and minimizes plugging of lines and burner tips

Burned Under Boilers

Eventually it was decided to burn the sludge under three of the plant boilers. These were of Foster-Wheeler make, equipped with soot blowers, had carbon steel tubes and carried a steam rating of 83,000 lbs. per hour at 450 psig. A home-made burner was developed, as shown in Fig. 1, similar to the familiar heavy fuel oil burner of the steam-atomizing type, and inserted in the Peabody gas ring burners with which the boilers were equipped.

The advantage of the Peabody burner with a sludge burner inserted in the center was that the sludge was consumed in a whirling cone of gas flame. This already had been found essential in avoiding soot and fumes. Construction of the sludge gun allowed for inspection, maintenance or repair without disturbing the gas burner. Air flow for optimum mix could be readily adjusted with either or both fuels in use.

The first sludge burners were steel, which swiftly corroded to uselessness. Replacements were made of cast iron, which had a longer life, and ultimately numerous alloys were tried.

A host of troubles followed. The system comprised a 20 by 20-ft. fuel oil tank as a combination storage and surge vessel and a 6 by 4 by 6 steam reciprocating circulating and feed pump for delivering the sludge to the burners. Chunks of heavy sludge stuck the pump valves open, plugged burner tips, and solidified in the burner supply line as well as in the line from the treating plant. Although unsuspected at first, solidification also occurred in the surge tank. Air blowing was tried to keep the tank contents agitated, but this only made matters worse.

In desperation after the stock tank filled completely with heavy mate-

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rial, which ultimately had to be dug out by hand, fuel oil was added to the sludge. Still lumps consolidated in the tank, plugged lines and burners, and formed deposits on furnace walls, floors, and tubes.

Intermediate storage, i.e., the surge tank, then was discontinued in favor of direct feed from the acid treating units to the burners at the same rate as it was produced.

This did not work well, either. In the first place, serious surges in flow developed because of the pulsating flow from the reciprocating pump. This was mitigated by installation of a Quimby screw pump. However, the system still was unstable because the burners received slugs of acid, then oil, then sludge.

Burner tips were unsatisfactory also, and cast iron, stainless steel, and finally red brass were tried. Brass seemed the most satisfactory. A small surge tank—the present 6 ft. by 9 ft. vessel—also helped, and the system operated fairly well until about 1944.

Spent Alkylation Acid Burned

During the war, consumption of sulfuric acid at the plant climbed materially. While "spent" alkylation acid was revivified and re-used, it became necessary on occasion to dispose of approximately 35 tons per day of 87% acid, plus 200 tons daily of acid sludge. To handle this amount of material, changes were made in the burner design. Successive composition changed from brass to K-monel in 1942, and back to carbon steel by 1944. Experimentation with burner tip materials and designs continued.

Once more trouble occurred. Due to the increased quantity of acid being burned, complaints of soot and fumes again were heard from nearby residents. These were more serious than ever before because wartime had brought with it development of an extensive residential district in the vicinity of the refinery, located where prevailing winds would carry particles in that direction. Moreover, complainants said the sooty particles carried a considerable acid content which ate holes in the family wash, corroded window screens, and damaged roofs and paint.

This was not all. The acid "raised the devil" with the pump, eroding and corroding the screw impeller, packing, and even the bearings. Leaks were so numerous and frequent that concrete paving around the pump had to be replaced. Line corrosion also was experienced, plus the usual occurrence of plugged lines and burner tips.

All kinds of experiments were then tried. Hastelloy burner tips were installed to be sure erosion was not altering flame patterns and interfering with proper dispersion of the sludge. Different designs of commercial and home-spun fuel oil guns and tips were tested. Some Bunker "C" was added to the fuel to minimize slugs of acid.

Net result of all this work was evidence that burner juggling was not the answer to the sludge disposal problem. The difficulties seemed to center largely in the non-homogeneous nature of the acid sludge and its tendency to solidify on standing, with or without agitation.

Homogenizing System Developed

Finally it was decided to try some kind of a milling or homogenizing operation. A vertical type mill marketed by the Volcanic Specialties Co., Alliance, O., shown in Fig. 2, was installed early in 1946. This device consists of a vertical, cylindrical shell of steel containing a central shaft on which are mounted a number of solid, toothed wheels. The shaft is driven by any convenient means; in this case a 50-hp. motor.

A close fit between shell and toothed wheels is maintained. This tends to grind sizable chunks of sludge into small particles as the sludge is squeezed through the mill by pump pressure. The mill has both a grinding and a mixing effect, producing a relatively homogeneous effluent. The shaft is supported by a bearing at the inboard end only, with conventional packing just ahead of this to keep the bearing clean.

The arrangement developed is shown in the diagram of Fig. 3. Sludge from the surge tank is picked up by the 50-gpm. screw pump and enters the bottom of the mill, emerges from the top and is circulated to the burners and back to the surge tank. A by-pass is provided when the mill is taken out of service for maintenance, and a spare pump is available also.

The unit first went into service in May, 1946. Mill packing got excessively hot within the first 30 minutes and the unit was cut out of the line for investigation. The acid had attacked the packing. When it went back into service three days later, this trouble continued and the shell of the mill also grew quite hot. A satisfactory arrangement for injecting oil into the lantern rings finally was evolved to keep acid out of the packing and to prevent it from entering the bearings. No further serious trouble has been experienced with the mill.

At first the boiler operators were convinced the new "gadget" was good for nothing; just another source of annoyance. However, they quickly found that complaints from soot and fumes are a thing of the past—except when the mill is out of service for periodic maintenance. They also found the combustion was much less erratic and that deposits on tubes and boiler settings had decreased. Now the operators say they would not be without the mill, unless burning of sludge under boilers were to be eliminated also.

It has been noted, however, that fumes still attack boiler settings and stacks. Stack corrosion can be controlled by guniting when necessary, and acid-resistant firebrick and ceramic will help solve the corrosive attack on boiler settings. Other than this there appears no ready solution to the attack of acid fumes. For burner tips, it appears that Hastelloy "B" alloy best resists corrosion and erosion but is not perfect.

In short, the present system appears to be the best solution at the Pan American refinery to the difficult problem of disposing of acid sludge in the least expensive and troublesome manner. Company officials say, however, that if anyone has a better system to propose they are willing to consider it.

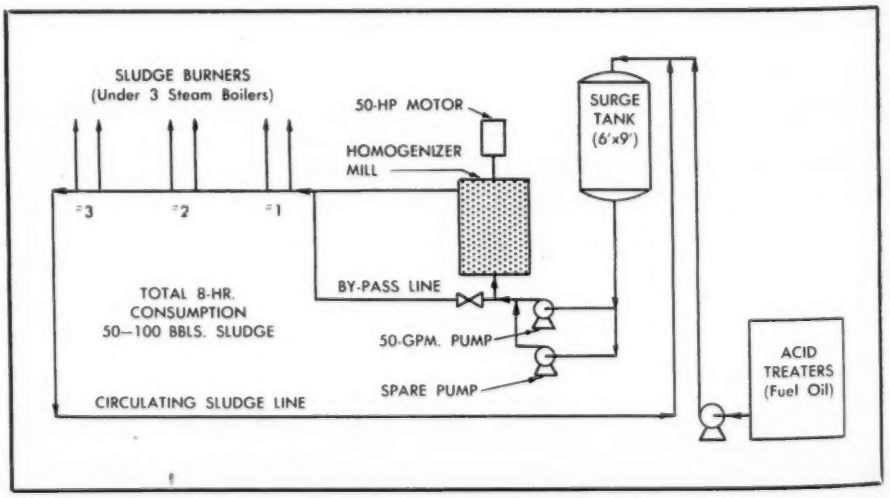

Fig. 3—Flow diagram for acid sludge disposal system, showing arrangement of pumps, surge tank and pulverizing mill

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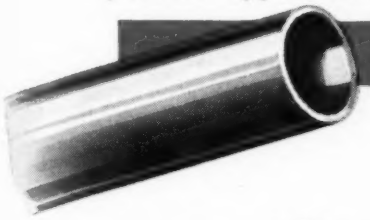

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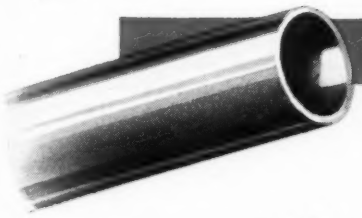
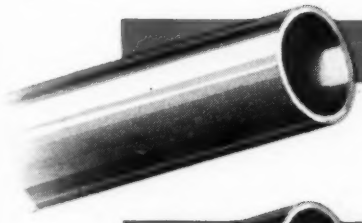
tubes are used extensively for steam condensers where fresh water is available.



RED BRASS

is used in Condensers and Heat Exchangers where it is necessary to combat dezincification and where water is low in acidity.



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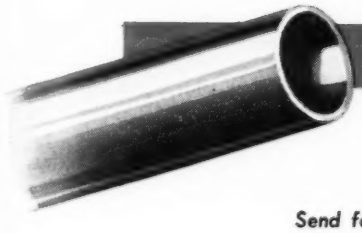

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Method for Correlating Thermal Reforming Yield Data with Operating Conditions

By HAROLD F. TIGHE
Shell Oil Co., Inc., Wood River, Ill.

Reforming yields and octane number increases are plotted versus factors representing the per cents of charge stocks cracked, factors that are calculated from operating conditions and the paraffinicities of the charge stocks. The inter-relation of yields with octane number increases and paraffin contents of charge stocks also provide a simple and rapid method for approximating product yields for operating control purposes when the charge stock is an ordinary straight run naphtha within the boiling ranges studied.

A METHOD has been developed for correlating reforming yields with operating conditions which interrelates temperature, time and reaction rates. Allowance is made for paraffins and non-paraffins reacting at different rates and for the continual decrease in the relative quantities of the parent materials as the reaction progresses. The final expression is called the "Reforming Number" and is designated by *S*.

Yield data from naphthas of widely varying paraffinicity and test runs over a wide range of severities were found to fall on a common curve when plotted against *S*. A distinct relationship is also shown between octane number increase, paraffinicity of charge and *S*. This latter feature offers a possibility of predicting the octane number increase to be expected in existing reformers when charging an unknown straight run naphtha if it is within the boiling ranges studied and its paraffinicity is known. It also provides a simple and rapid method for approximating yields for operating control purposes, i.e., if the paraffin content and the octane number in the charge stock have been established, the increase in the octane number due to the reforming operation will determine *S* and, consequently, the yields of the various components.

Discussion

Methods recently proposed for correlating reforming data fall into two general types, differentiated by the manner of calculation:

1) Yields are correlated with a value that is obtained by the multiplication of the average coil temperature above a fixed base temperature times residence time.

2) Yields are plotted against factors which are determined by integrating the area under a rate-time diagram.

The first case entails the assumption that the coil temperature is a straight line function of rate of cracking. Although some success was obtained by this type of correlation, it was probably due to the parallelism of the various temperature-time curves. The method fails entirely when the slopes are varied to any great extent, i.e., curves enclosing equal areas but widely different transfer temperatures would not represent equal amounts of cracking due to the rapid acceleration of the rate of cracking with respect to temperature.

In the second case, the effect of the depletion of the various charge stock components on the rate of cracking is not taken into account, nor has the rate of cracking of a charge stock been established, since it is treated as a single component in a first order reaction with a constant concentration of uncracked stock. The instantaneous rate of cracking of a naphtha may be expressed as the sum of the rates of the individual components multiplied by their respective fractional parts of the total uncracked stocks. Considering naphtha, the components with higher rates of cracking are depleted faster than others as cracking proceeds, which reduces the total rate, because the concentrations of the faster cracking components in the charge stock are decreased. The half-life of paraffins in a reforming naphtha at 1000° F. is approximately 12 sec. (1) while substituted aromatics at the same temperature have a half-life of about 30 sec.(2). It will be seen from the above that depletion of individual components has a marked effect on the amount cracked; therefore, the rate of cracking of a multicomponent naphtha cannot be established if it is treated as a single component with a constant concentration.

It is the purpose of this paper to submit a method for correlating reforming data in which the nature and amount of depletion of a charge stock is partially taken into consideration.

Method for Correlation

The method for correlation, the derivation of which is appended to this paper, is as follows:

Yields are plotted against terms that are calculated from the operating conditions and the analyses of the charge stocks. These terms will be designated by *S* and will be called reforming numbers. *S* is calculated as follows: (For more detailed explanation see derivation.)

1) The coil temperature in °F. is plotted versus cubic feet of coil volume divided by the intake in barrels per minutes.

2) There is established a constant temperature line of 900° F. (It is assumed that no cracking occurs below 900° F.)

3-a) If plot is a straight line above 900° F., the following form is used:

$$R = \frac{1.035^{\Delta T} - 1}{\ln 1.035^{\Delta T}}$$

3-b) If it is not a straight line, the plot may be divided into shorter approximate straight lines and the following forms used:

$$R_1 = \frac{1.035^{\Delta T_1} - 1}{0.0344 \Delta T_1 / Z_2}$$

(where line segment intersects 900° F. base line)

$$R_2 = \frac{1.035^{\Delta T_2} - 1.035^{\Delta T_1}}{0.0344\ m_2}$$

(where line segment does not intersect 900° F. base line)

The values of R_1 and R_2 are added and the sum divided by the total change in *Z* above 900° F.; the resulting value is equal to *R*.

where:

R = the k at the mean effective temperature of the reaction.

k = reaction velocity constant at temperature T divided by the velocity constant at 900° F.,
T = temperature in °F.
$\Delta T_1 = T_1 - 900$,
Z = time factor—cu. ft. of coil volume/bbl. of charge per min.,
m = slope of temperature-time diagram $(\Delta T/\Delta Z)$.

4) K is solved for in

$$K = R^{\left(0.0020 + \frac{M-126}{2} \times 10^{-4}\right)}$$

where:

K = reaction velocity constant for paraffins at the mean effective temperature of the reaction,
M = molecular weight of the charge stock.

5) t is solved for in

$$t = 2.3 \Delta Z \ (P/T_a)$$

where:

t = time in seconds,
ΔZ = total change in Z above 900° F.,
P = outlet pressure in psia,
T_a = average temperature above 900° F. in °Rankine from temperature-time plot.

6) S is solved for in

$$S = \frac{p(e^{Kt}-1) + (1-p)(e^{Kt} - e^{0.6Kt})}{e^{Kt} \times 10^{-2}}$$

where:

p = fraction of paraffins in charge stock,
S = reforming number = fraction cracked times 100.

In the above method it was assumed that the rates of cracking of the main components of a virgin naphtha (paraffins, alkylated naphthalenes, and alkyl aromatics) act as in a first order reaction and double themselves for every 20° F. rise in temperature. While there are very good data available on paraffin velocity constants [1], the value of the other components is still in doubt. However, from data published[1], it is very probable that for most of the saturated hydrocarbons found in the naphtha boiling range, the slopes of the log K versus T diagrams are approximately the same.

It was also assumed that the rates of cracking of alkylated naphthenes and alkyl aromatics in the same boiling range are approximately equal. The value of

$$n = \frac{K(\text{non-paraffins})}{K(\text{paraffins})} = 0.4$$

was calculated from experimental data and checks very closely with data published for alkyl aromatics in the naphtha boiling range[2]. This appears to make valid the assumption of equal reaction velocities for the non-paraffins because of the small percentage of alkyl aromatics that were present in the charge stock.

It was further assumed that the aromatic to non-aromatic ratio varies with boiling range in a fixed relationship irrespective of charge stock, i.e., for any two stocks

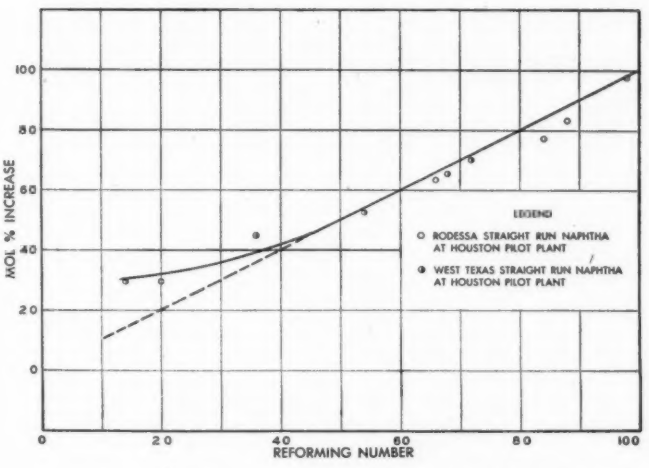


Fig. 1—Molar increase accompanying reforming

A and B of different paraffin content, the paraffin to non-paraffin ratios, n_A and n_B, are related by

$$n_A/n_B = C$$

where C is a constant essentially independent of boiling range.

For example, if stock A is more paraffinic than B, this correlation would predict A to more readily cracked, whereas if the paraffins in A are concentrated in the low boiling range, while those in B occur primarily in the high boiling range, B quite likely would be equally, if not more, readily cracked.

In the case where C varies greatly when compared with naphthas correlated herein, it may be necessary to evaluate n and the reaction velocity constant K for narrow boiling fractions of the naphthas, and thus calculate K and n weighted for component distribution.

Throughout the derivation, the polymerization and the secondary cracking of the cracked products were neglected. The main purpose was to establish a means by which the depth of cracking could be determined solely for the purpose of correlation. However, from experimental data it can be stated that for all practical purposes virgin naphthas act as in a true first order reaction. In Fig. 1, the mol % increases are plotted against the reforming numbers, and for values above 50 they were numerically approximately equal. Under 50 the divergence may be the result of the assumption of no cracking under 900° and the error introduced in the calculation of t, an error that decreases as the value of S approaches 60. All virgin naphthas contain naphthenes and aromatics having side chains of varying length. Those constituents having long side chains are very susceptible to cracking; consequently, they would crack earlier in the reaction than would be predicted by the average side chain length. As the reaction proceeds, the concentration of these constituents decreases and, since the short side chain molecules are relatively stable, this results in a lower rate of cracking. This effect, along with the unassumed refractoriness of the few unsubstituted ring compounds and the reduction of the error in the calculated value of t, would explain the convergence of the two lines around the 50% point.

Although pressure and transfer temperature have an effect on the unsaturate content, they do not change appreciably the total molar increase. From experimental data, the loss in olefin content (C_4 = and C_5=) due to an increase in pressure or a change in transfer temperature is supplemented by an increase in the C_1 or C_2 fraction. This suggests that in the mechanics of a condensation reaction at a high temperature and pressure, one of the predominant reactions is the splitting of each of the molecules either during or immediately prior to the condensation. This may result in the cyclozation to aro-

THE AUTHOR

Harold F. Tighe was born in Martins Ferry, Ohio and was graduated from the Georgia School of Technology in 1944 with a B. S. degree in Chemical Engineering.

Upon graduation he joined Shell Oil Company, Inc. in their Wood River Refinery as a Technologist specializing in cracking operations, a position he still holds.

matics[4]. In other words, condensation is carried out without a noticeable decrease in the number of molecules. From the experimental data, this appears to be the logical explanation due to the negligible effect pressure exerts on the first order reaction velocity.

The yield data for various fractions are plotted versus Reforming Number in Figs. 2 through 7.

In Fig. 2 the increases in ASTM octane numbers from pilot plant data are correlated with reforming numbers and the paraffinicities of the charge stocks. A line joining the data from Wood River's Dubbs 1 was found by interpolation with the other data to have a paraffin content for the charging stocks of 39% while the actual analyses ranged from 37 to 41. Therefore, it is very probable that

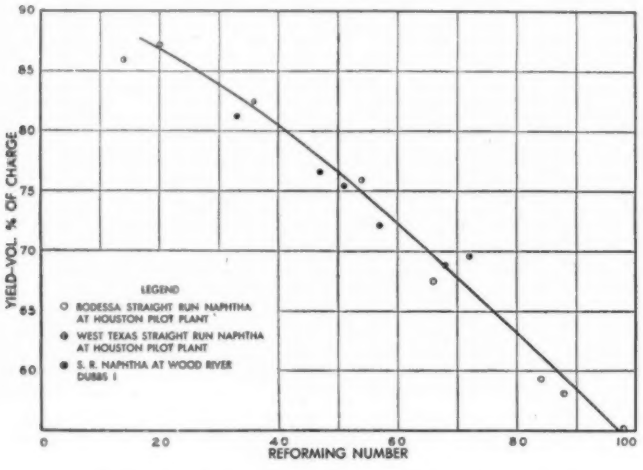

YIELD-VOL. % OF CHARGE
REFORMING NUMBER
LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER DUBBS 1

Fig. 2—Yield of C_6 + fraction vs. Reforming Number

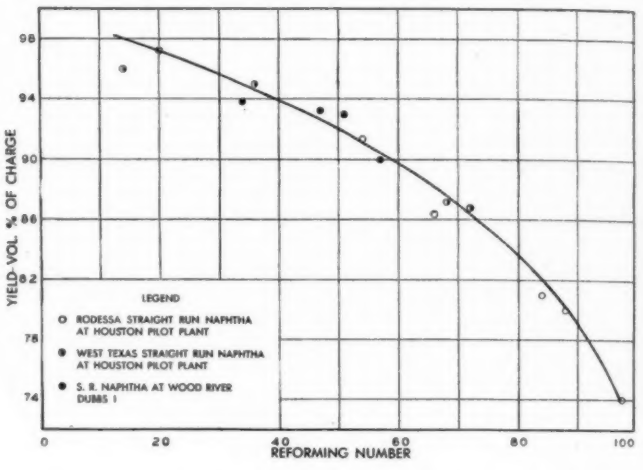

YIELD-VOL. % OF CHARGE
REFORMING NUMBER
LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER DUBBS 1

Fig. 3—Yield of C_4 + fraction vs. Reforming Number

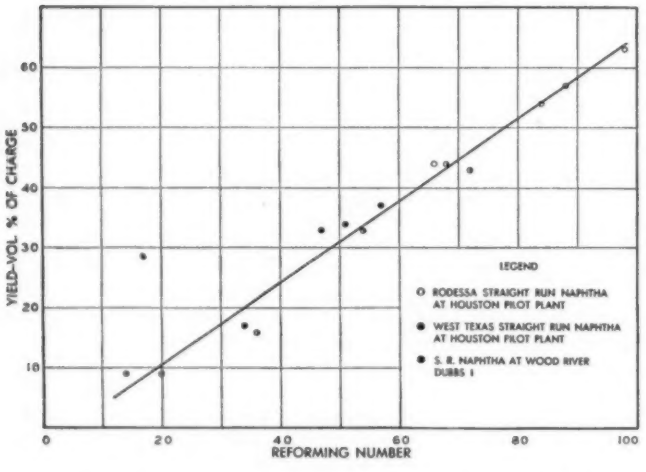

YIELD-VOL. % OF CHARGE
REFORMING NUMBER
LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER DUBBS 1

Fig. 4—Yield of C_5 and lighter fraction vs. Reforming Number

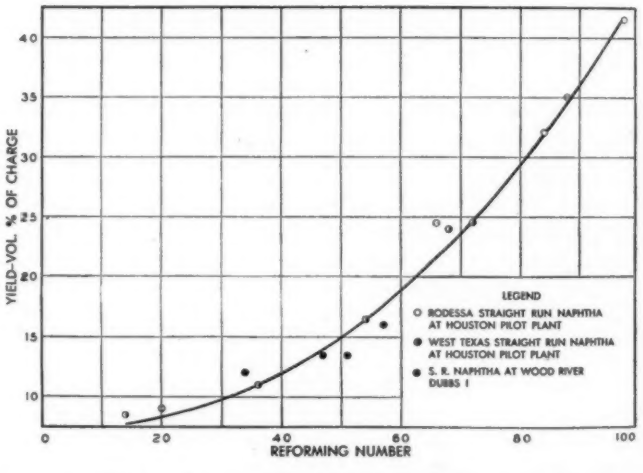

YIELD-VOL. % OF CHARGE
REFORMING NUMBER
LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER DUBBS 1

Fig. 5—Yield of C_3 and lighter fraction vs. Reforming Number

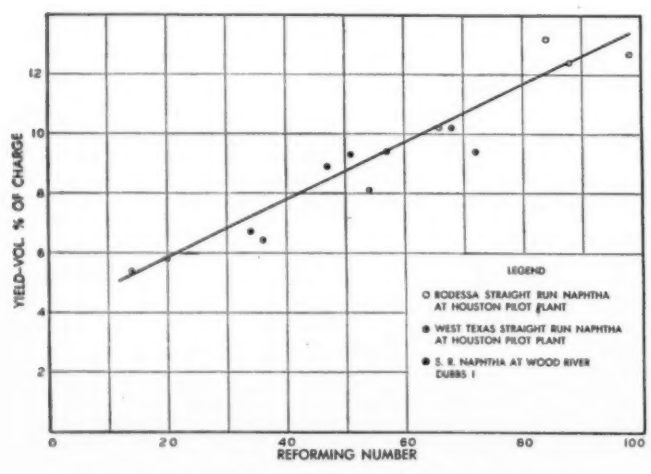

YIELD-VOL. % OF CHARGE
REFORMING NUMBER
LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER DUBBS 1

Fig. 6—Yield of C_4 fraction vs. Reforming Number

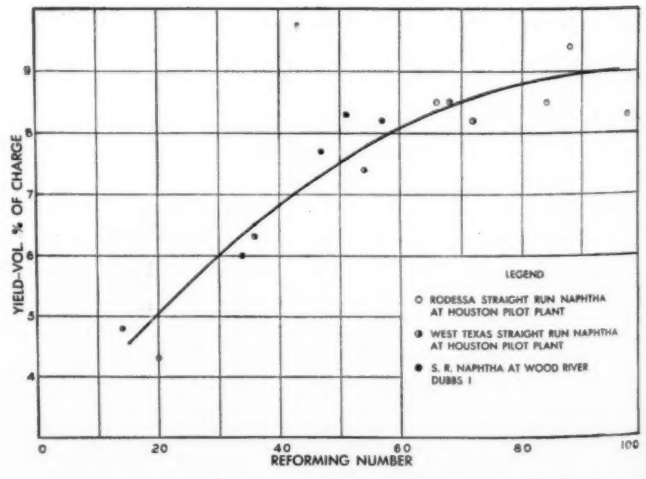
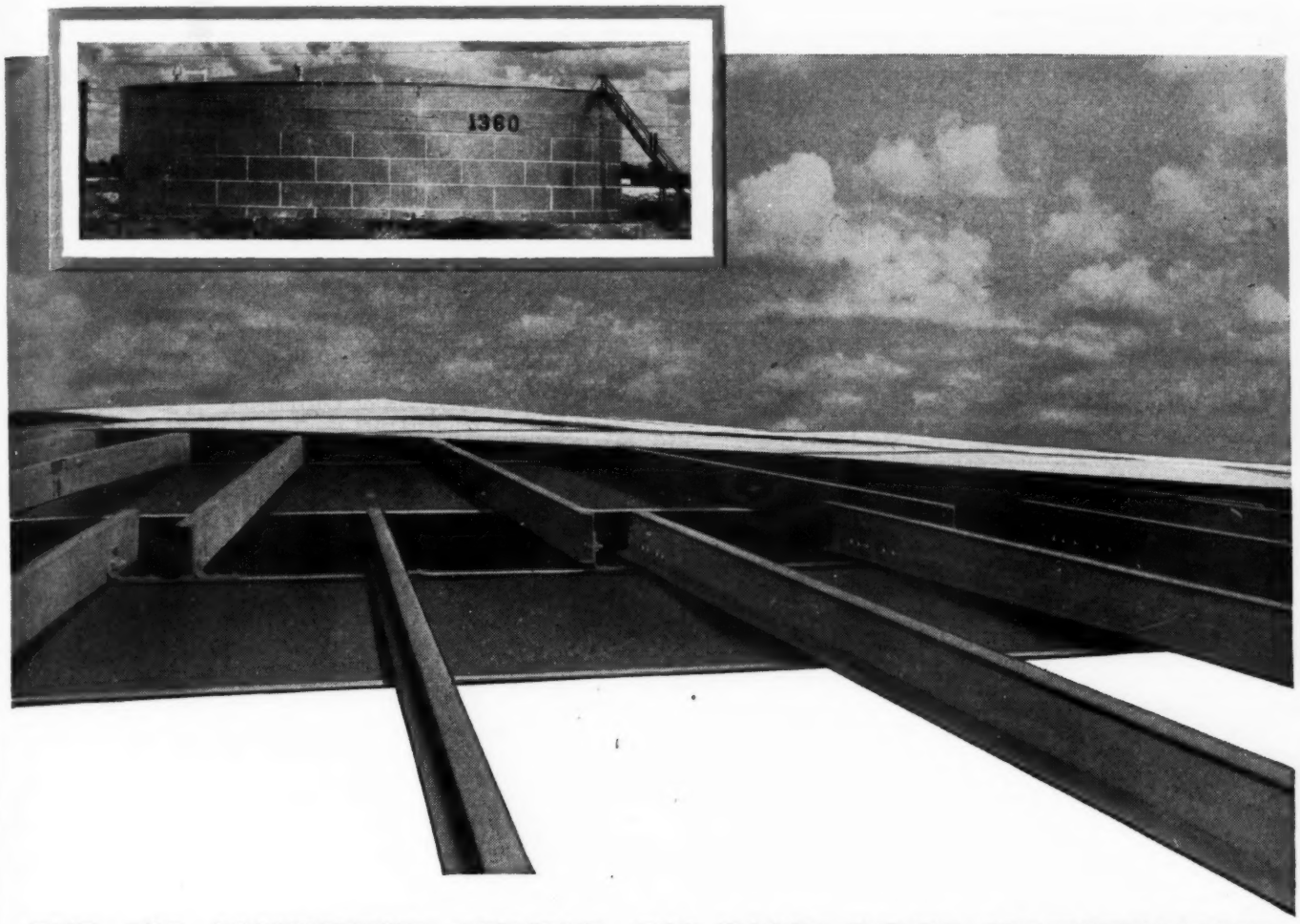

YIELD-VOL. % OF CHARGE
REFORMING NUMBER
LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER DUBBS 1

Fig. 7—Yield of C_5 fraction vs. Reforming Number



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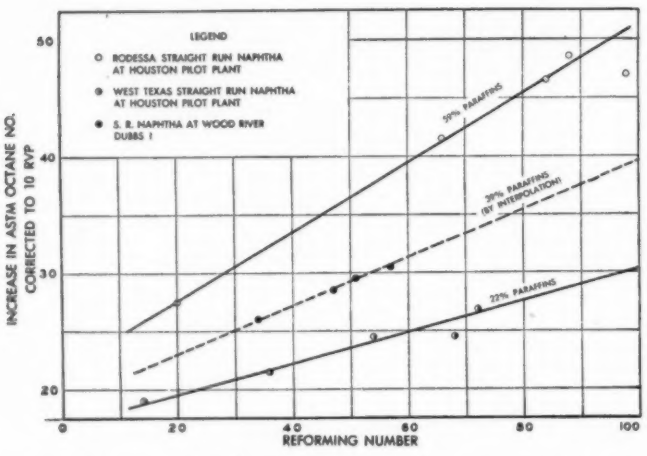

LEGEND
RODESSA STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
WEST TEXAS STRAIGHT RUN NAPHTHA AT HOUSTON PILOT PLANT
S. R. NAPHTHA AT WOOD RIVER
INCREASE IN ASTM OCTANE NO. CORRECTED TO 10 RVP
REFORMING NUMBER
50% PARAFFINS
39% PARAFFINS (BY INTERPOLATION)
22% PARAFFINS

Fig. 8—Increase in ASTM octane number accompanying reforming

the octane number increases for any ordinary straight run naphtha may be predicted via the interpolation method. The prediction of the octane number may be erroneous when applied to the straight run charging stocks having molecular weights outside the range studied in this report. This is particularly true of the lower molecular weight charging stocks, since thermal reforming of the lighter hydrocarbons having higher octane numbers results in a smaller octane number improvement compared with the higher boiling stocks due to the smaller differential between the octane numbers of the cracked and the uncracked feed components remaining in the reformed gasoline. It is quite possible that a method might be devised for the correlation of octane number increases with reforming numbers over a wider range by employing octane number and molecular weight of the charge stock as additional variables.

The unsaturate yields were not correlated. It has been found by experience that the amount of unsaturates in a hydrocarbon class produced from the same boiling range charge stock is usually constant for any one pressure, e.g., the per cent butylenes in the butane fraction will vary between 60 to 40% as the pressure changes from 500 to 1200 psi.

The individual yields of C_1 to C_3 would have no significance in a correlation with S because of the different characteristics of the substituted ring compounds in various charging stocks; however, the total C_3 and lighter fraction would be of significance because it is somewhat of a measure of the amount of cracking and therefore may be correlated.

The method presented in this paper should be valid for ordinary straight run charging stocks within the boiling ranges studied, having values of Kt ranging from 0.5 to 7.5. Since there are no experimental data available for values of Kt higher than 7.5, it is not possible to predict whether secondary cracking and condensation would continue to balance so as to simulate a first order reaction.

Should the molecular weight of a charging stock deviate appreciably from the range studied in this report, the calculation of the reforming number may entail a slightly different approach. The calculation would remain the same through step 3, i.e., through the calculation of R. However, since the average length of the side chains on the substituted naphthenes and aromatics would be changed appreciably, the value of n might also change significantly. It would be necessary, therefore, to determine a new value of n corresponding to the desired boiling range before the calculation could be completed. Further, due to the difference in the size of the average molecule, somewhat different product yields might be observed. It should be possible, however, to predict with a fair degree of certainty the yields that would be obtained. The upper limit for the molecular weight of a charge stock at which a reforming number could be calculated with average accuracy would be determined by the point at which an appreciable amount of secondary cracking would occur.

For the calculation of R in the majority of reforming operations it should be possible to represent the temperature-time plot with a straight line, thus facilitating a quicker method by the use of the more simple form. Neither equation is cumbersome, however, when experience has been obtained by calculating a few values on a log-log slide rule. If, for any reason, still more accuracy is demanded in the calculation, it may be integrated graphically.

Derivation of Correlating Equation

Since the temperature coefficient of the reaction velocity constant of the main components of an ordinary reforming charge stock is assumed to be a constant (doubling for every 20° F. rise in temperature), the velocity constants of the components may be expressed as follows:

$$k=\frac{K'_T}{K'_{900}}=2^{(T-900)/20} \quad \ldots\ldots (1)$$

where:

k = reaction velocity constant at temperature T/velocity constant at 900° F.,

K' = reaction velocity constant for any one main component,

T = temperature in °F.

If temperature in °F. is plotted versus tube volume divided by feed rate in barrels per minute and the curve above 900° is a straight line, then the temperature above 900° may be expressed in terms of time by the equation:

$$T=900+mZ \quad \ldots\ldots (2)$$

where:

m = the slope of the line,

Z = tube volume (cu. ft.)/intake (bbl./min.).

Substituting Equation 2 in Equation 1:

$$k=2^{(900+mZ-900)/20}=2^{mZ/20} \quad \ldots\ldots (3)$$

Multiply both sides by dZ and integrate between Z_1 and Z_2:

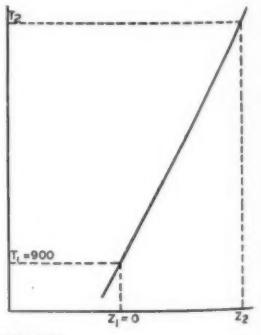
$$\int_{Z_1}^{Z_2} k\,dZ=\int_{Z_1}^{Z_2} 2^{mZ/20}dZ \quad (m \text{ is constant})$$

$$k(Z_2-Z_1)=\frac{2^{mZ_2/20}-2^{mZ_1/20}}{\ln 2^{m/20}} \quad \ldots\ldots (4)$$

By selective choosing of the limits, Z_1 and Z_2, the equation may be further simplifed:

Let $Z_1=0$ = time at 900°,
Z_2 = time at temperature T_2,
$\Delta T=T_2-900$
then $mZ_2=\Delta T$, and:

$$m=\Delta T/Z_2 \quad \ldots\ldots (5)$$



Substituting in Equation 4:

$$k(Z_2-0)=\frac{2^{mZ_2/20}-2^{mZ_1/20}}{\ln 2^{m/20}}$$

$$=\frac{2^{\Delta T/20}-1}{\ln 2^{\Delta T/20Z_2}}$$

Since $2^{1/20}=1.035$, the equation becomes:

$$kZ_2=\frac{1.035^{\Delta T}-1}{\ln 1.035^{\Delta T/Z_2}}=\frac{1.035^{\Delta T}-1}{\frac{\Delta T}{Z_2}\ln 1.035}$$

Substituting the numerical value of ln 1.035 and solving for k, we get:

$$k=R=\frac{1.035^{\Delta T}-1}{\ln 1.035^{\Delta T}} \text{ or } \frac{1.035^{\Delta T}-1}{0.0344\,\Delta T} \quad \ldots\ldots (6)$$

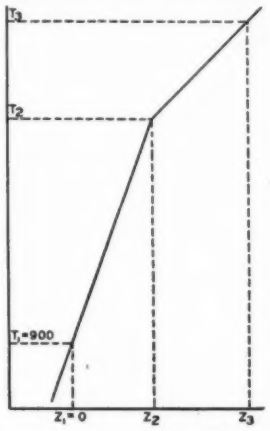
where R = the k at the mean effective temperature of

the reaction, i.e., the mean ordinate in the rate-time diagram.

If the T versus Z plot cannot be represented by one slope, it may be divided into a series of 2 or 3 lines with different slopes. The $\int kdZ$ under each line may be calculated, added together, and divided by the total change in Z.

Thus, for the line that intersects the 900° base line:

$$\int kdZ=\frac{2^{m_1Z_2/20}-2^{m_1Z_1/20}}{\ln 2^{m_1/20}}=\frac{1.035^{\Delta T}-1}{0.0344\dfrac{\Delta T_1}{Z_2}} \quad \ldots\ldots\ldots (7)$$



For the line from T_2 to T_3:

$$\int kdZ=\frac{2^{m_2Z_3/20}-2^{m_2Z_2/20}}{\ln 2^{m_2/20}}=\frac{1.035^{\Delta T_2}-1.035^{\Delta T_1}}{0.0344^{m_2}} \quad \ldots\ldots\ldots (8)$$

where:

$$\Delta T_1=T_2-900;\ m_1=\frac{\Delta T_1}{Z_2-Z_1};\quad \Delta T_2=T_3-900;\ m_2=\frac{T_3-T_2}{Z_3-Z_2};$$

$$m_2Z_3-m_2Z_2=\Delta T_2-\Delta T_1$$

then:

$$\int_{Z_1}^{Z_3} kdZ=k(Z_3-Z_1)=kZ_3$$

$$=\frac{1.035^{\Delta T_1}-1}{0.0344\dfrac{\Delta T_1}{Z_2}}+\frac{1.035^{\Delta T_2}-1.035^{\Delta T_1}}{0.0344m_2}$$

and:

$$k=R=\frac{1.035^{\Delta T_1}-1}{0.0344\dfrac{\Delta T_1}{Z_2Z_3}}+\frac{1.035^{\Delta T_2}-1.035^{\Delta T_1}}{\dfrac{0.0344m_2}{Z_2}}$$

From Equation 6 and literature data:[1]

$$K=R\left(0.0020+\frac{M-126}{2}\times 10^{-4}\right)$$

where K=reaction velocity constant for paraffins[1] at the mean effective temperature.

The total amount cracked may be expressed as the sum of the individual components. For this purpose the kinetic equation for a first order reaction at constant volume is applied. As is shown below, this is not exact, but a more rigorous equation is much too cumbersome to use.

For paraffins at constant temperature:

$$\frac{-dq}{dt}=Y_p=K_q \quad \ldots\ldots\ldots (10)$$

where:

Y_p=rate of cracking paraffins,
q=amount of paraffins,
t=time,
C=concentration,
$_o$=zero time

Equation 10 is not exact, because

$$\frac{q_o}{q}\neq\frac{Cq_o}{Cq}$$

The inequality arise[3] since:

$$\frac{Cq_o}{Cq}=\frac{q_o}{V_o}\cdot\frac{V}{q} \text{ and } V_o\neq V$$

The inequality of the initial and final volumes is due both to the molar increase due to cracking and to the drop in pressure through the cracking coil.

Returning to Equation 10:

$$-dq/dt=Kq$$
$$-dq/q=Kdt$$

Integrating between limits q_o, q and o, t:

$$\ln\frac{q_o}{q}=Kt$$
$$q/q_o=e^{-Kt}$$

$$q=q_oe^{-Kt} \quad \ldots\ldots\ldots (11)$$

Substituting Equation 11 in Equation 10:

$$Y_p=Kq_oe^{-Kt}$$

$$\int_o^t Y_pdt=Kq_o\int_o^t e^{-Kt}dt=\frac{q_oKe^{-Kt}}{-K}\Big|_o^t$$

$$Y_pt=-(q_oe^{-Kt}-q_o)=q_o(1-e^{-Kt})$$

$$Y_pt=\frac{q_o(e^{Kt}-1)}{e^{Kt}} \quad \ldots\ldots\ldots (12)$$

This is equivalent to amount of paraffins cracked.

Since it was assumed that all components of the naphtha had the same temperature coefficient of reaction velocity, then at any temperature:

$$\frac{K \text{ (non-paraffins)}}{K \text{ (paraffins)}}=n$$

where n is a constant to be determined experimentally.

The reaction velocity constants of the non-paraffins are assumed to be equal.

Let p=fraction of paraffins in charge stock,
S=Reforming Number=fraction of the total feed cracked multiplied by 100.

Then, substituting in Equation 12:

$$S=\frac{\dfrac{p(e^{Kt}-1)}{e^{Kt}}+\dfrac{(1-p)(e^{nKt}-1)}{e^{nKt}}}{1\times 10^{-2}}$$

To simplify the complex fraction in the numerator, the least common denominator is e^{Kt}.

Simplifying:

Note that $e^{Kt}=(e^{nKt})(e^{(1-n)Kt})$.

$$S=\frac{p(e^{Kt}-1)+(1-p)(e^{Kt}-e^{(1-n)Kt})}{e^{Kt}\times 10^{-2}} \quad \ldots\ldots\ldots (13)$$

Two experimental runs with widely varying charging stocks and operating conditions (Runs 184 IV and 172 I: see data in tables) produced essentially the same yields* and the same molar increase. Therefore, $S_1=S_2$. Substituting data for these runs in Equation 13, the following equations are obtained for S_1 and S_2:

$$S_1=\frac{p_1(e^{.0021R_1t_1}-1+(1-p_1)(e^{.0021R_1t_1}-e^{(1-n).0021R_1t_1})}{e^{.0021R_1t_1}\times 10^{-2}} \quad (14a)$$

$$S_2=\frac{p_2(e^{.0023R_2t_2}-1)+(1-p_2)(e^{.0023R_2t_2}-e^{(1-n).0023R_2t_2})}{e^{.0023R_2t_2}\times 10^{-2}} \quad (14b)$$

where p_1 and p_2 are obtained by analyses, and R_1, t_1, R_2 and t_2 are calculated from operating conditions, solving for n, the only unknown:

$$n=0.4$$

*Yields of C_1, C_2 and C_3 summed together, since individual yields are dependent on structure of feed stock components. Other fractions (C_4, C_5, etc.) are considered individually.

TABLE 1—Results of Reforming Runs in Houston Pilot Plant

	Charging Rodessa S.R. Naphtha					Charging W. Texas S.R. Naphtha				
Run No.	175 I	184 IV	183 I	177 I	184 II	144 I	144 IIB	159 I	172 I	154 I
Formula Factors:										
R	3.88	12.5	21.2	26.1	84.8	3.48	7.6	16.3	26.4	22.5
K	.00815	.0262	.0446	.0549	.178	.0080	.0175	.0375	.0607	.0517
Z	24	30	34	32	44	16	34	34	32	37
P	915	1215	1215	1215	615	915	915	765	765	915
T_a	1400	1417	1430	1430	1460	1391	1407	1415	1440	1423
t	36	59	66	63	42	35	51	42	40	53
e^{Kt}	1.342	4.7	19	32	1800	1.323	2.44	4.84	11.4	15.5
$e^{0.6Kt}$	1.193	2.5	5.9	8	90	1.183	1.71	2.54	4.3	5.2
S	20	66	84	88	98	14	36	54	68	72
Operating Conditions:										
Pressure, psig	900	1200	1200	1200	600	900	900	750	750	900
Feed rate, gal./hr.	1.53	1.49	1.50	1.57	1.51	1.49	1.39	1.52	1.54	1.53
Temperature Gradient, °F.:										
Tube no. 4 outlet	....	839	852	858	923	....	820	864	847	870
Tube no. 6 outlet	894	922	932	944	995	882	910	930	952	942
Tube no. 8 outlet	935	969	987	995	1037	928	957	972	992	992
Transfer	961	1006	1022	1032	1078	962	993	1007	1031	1029
Yields, vol.-% of feed:										
Methane	1.46	4.57	6.93	7.78	8.73	2.05	3.63	4.49	6.64	6.61
C_2	2.55	8.23	10.34	10.81	14.42	2.66	4.08	5.78	6.67	8.07
C_3	4.77	11.64	14.37	16.31	18.40	3.72	5.65	7.53	10.75	9.92
C_4 Olefins	2.55	4.88	6.19	5.45	7.57	2.50	2.71	4.22	4.85	4.37
C_4 Saturated	3.22	5.34	7.05	6.92	5.09	2.87	3.70	3.88	5.18	4.97
C_5	4.33	8.54	8.52	9.42	8.34	4.78	6.32	7.35	8.50	8.15
C_{5+}	87.22	67.52	59.32	58.05	55.11	85.87	82.36	75.77	68.79	69.60
TOTAL	106.10	110.72	112.72	114.74	117.66	104.45	108.45	109.02	111.38	111.69
Mol % Increase	29.82	61.76	77.60	83.35	97.80	29.70	44.83	52.40	65.57	70.14
ASTM Octane Number	49.1	63.3	69.3	71.5	69.6	66.8	69.3	72.5	74.3	74.8

TABLE 2—Properties of Stocks at Houston Pilot Plant

	Rodessa S.R. Naphtha	West Texas S.R. Naphtha
Gravity, °API @ °60 F	57.3	50.0
ASTM Octane No.	22.7	47.9
IBP, °F.	225	190
10%, °F.	264	254
50%, °F.	298	310
90%, °F.	350	370
E.P., °F.	401	408
Molecular Weight	128	132
Analyses of Feed Stocks		
Aromatics, %	10.6	16.7
Naphthenes, %	30.5	61.4
Paraffins, %	58.9	21.9

TABLE 3—Charging S.R. Naphtha at Dubbs 1, Wood River

Date	1-3-46	1-25-46	1-29-46	2-1-46
Feed Rate, b/d	7,200	10,100	10,100	8,100
Pressure, psig (outlet)	510	590	590	550
Temperature Gradient, °F:				
Floor to roof heating	825	900	875	885
Crossover	935	970	970	970
Roof to floor soaking	965	985	995	990
Transfer	970	995	1010	1000
Yields, Vol.-% of Feed:				
Methane	2.9	3.1	4.1	4.4
C_2	5.0	5.4	5.5	6.4
C_3	6.5	7.1	6.3	7.3
C_4	3.7	4.9	5.2	5.0
C_4 Saturated	3.0	4.0	4.1	4.4
C_5	6.0	7.7	8.3	8.2
C_{5+}	81.1	76.6	75.3	72.2
TOTAL	108.2	108.8	108.8	107.9
Increase in ASTM Octane Number	26	28.5	29.5	30.5
% Paraffins in Charge Stock	38	37	39	41

then substituting n in Equation 13 for any virgin naphtha charge:

$$S = \frac{p(e^{Kt}-1)+(1-p)(e^{Kt}-e^{0.6Kt})}{e^{Kt}\times 10^{-2}} \qquad (15)$$

The manner in which t is evaluated in this paper encompasses several assumption:

1) The molecular weight and specific gravity of the charge stock are assumed to be 130 and 6.5 lbs. per gal., respectively. However, a slight variance in these would not significantly change the final value.

2) The compressibility factor for the gases is assumed to be 0.75. This value should be sufficiently exact for most reforming operating conditions.

3) Since most of the cracking is usually experienced near the furnace outlet, the outlet pressure is used in the evaluation of t.

4) As the components of the charge stock are cracked, some factor must be employed to allow for the increase in the number of mols. The factor used is 1.5.

From the above assumptions, it can be seen that the calculated value of t equals the actual t in only a few cases. However, it was felt that a more exact method would be too cumbersome to justify its usefulness. The value of S at which t is most nearly exact is believed to be somewere around 60. Calculation of t follows:

$$t=\Delta Z\,(\text{cu. ft./bbl./min.})\times\frac{60\text{ sec.}}{\text{min.}}\times\frac{\text{gal.}}{6.5\text{ lbs.}}\times\frac{\text{bbl.}}{42\text{ gal.}}\times\frac{130\text{ lbs.}}{\text{mol.}}\times\frac{\text{mol.}}{359\text{ cu. ft.}}\times\frac{492}{T_a}\times\frac{P}{14.7}\times\frac{1}{0.75\,(\text{comp. factor})}\times\frac{1\,(\text{increase in volume})}{1.5\,(\text{due to molar increase})}$$

$$t=2.3\Delta Z\frac{P}{T_a} \qquad (16)$$

where:

Z = total change in Z above 900° F.,
P = outlet pressure in psia,
T_a = average temperature above 900° F. in ° Rankine (i.e., mean ordinate of time-temperature diagram; visual estimation would be sufficiently accurate.)

Acknowledgment

The author gratefully acknowledges the criticisms and suggestions of Mr. Lawson E. Border and Mr. Donald W. Miller, both of Shell Oil Company, Inc.

References

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Nomenclature

k = reaction velocity constant at temperature T/velocity constant at 900° F.
K' = reaction velocity constant for any one main component.
K = reaction velocity constant for paraffins at the mean effective temperature of the reaction.
R = reaction velocity constant at the mean effective temperature/velocity constant at 900° F.
T = temperature in °F.
Ta = average temperature above 900° F. in °Rankine from time-temperature plot (mean ordinate).
ΔT = T—900.
Z = time factor=cu. ft. of coil volume/bbl. of charge/min.
m = slope of time-temperature diagram ($\Delta T/\Delta Z$).
t = time in seconds=total ΔZ above 900° $\times$ $2.3P/T_a$
P = pressure in psia.
S = Reforming Number.
p = fractional part of paraffins in charge stocks (weight analyses should be accurate enough).
Y_p = rate of cracking of paraffins.
q = amount of paraffins.
C_q = concentration of paraffins.
V = volume of reaction space.
$_o$ = zero time.

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Normal Butane
Iso-Butane
Propane
Hexane
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WHERE CAUSTICS CAUSE CORROSION

TEST No. 1

Location: Reboiler of unit used to regenerate caustic solution for removal of mercaptans. Composition of aqueous solution entering tower: ½% sodium hydroxide, 10% sodium phenolate, 3% sodium sulfide, plus 0.07 mg. per 100 cu. cm. of the liquid as sodium mercaptides. Average temperature: 255° F. Duration of test: 131 days.

Material	Corrosion Rate, Inch per Year	
Monel	0.001	
Nickel	0.024	
Inconel	0.0001	
Metal A	0.025	
Metal B	0.004	(a)
Metal C	0.020	(b)
Metal D	0.017	

(a) Pitted to max. depth of 0.002 inch during test.
(b) Pitted to max. depth of 0.012 inch during test.

TEST No. 2

In reboiler of unit used to regenerate caustic potash solution. Composition: 2.5% potassium hydroxide, 37.8% potassium isobutyrate, 5.5% potassium sulfide, 1.9% potassium mercaptides, 2.1% potassium carbonate. *Test A:* Immersed in boiling liquid at upstream side of overflow weir. *Test B:* Suspended in vapor at downstream side. Average temperatures: 286° F. Duration of test: 140 days.

Material	Corrosion Rate, Inch per Year TEST A	TEST B
Monel	0.003	0.002
Nickel	0.022	0.016
Inconel	0.001	0.002
Metal A	0.015	0.012
Metal B	0.038	0.019
Metal C	(c)	0.012
Metal D	0.040	0.014

(c) Completely destroyed. Original thickness 0.062 inch.

TEST No. 3

Plant Corrosion Test in bottom of regenerator tower used to regenerate potassium hydroxide solution used to remove mercaptans. Composition of solution entering tower: 12.5% potassium hydroxide, 19% potassium isobutyrate, 28% alkyl phenolate, 0.4% mercaptans and 0.8% sulfides. Average temperature: 370° F. Duration of test: 276 days.

Material	Corrosion Rate, Inch per Year	
Monel	0.0007	
Nickel	0.0010	
Inconel	0.0005	
Metal A	0.012	
Metal C	0.0023	(d)
Metal D	0.006	

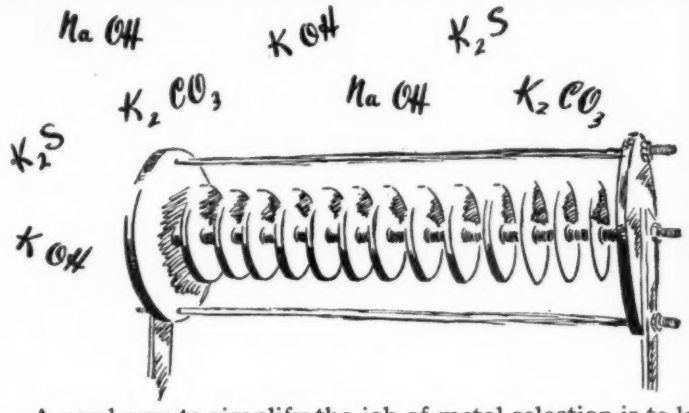
(d) Pitted to max. depth of 0.004 inch during test.

TEST No. 4

Plant Corrosion Test in vapor section of regenerator tower used to regenerate caustic solution used to remove mercaptans. Composition of solution entering tower: 13.2% sodium hydroxide, 0.3% sulfide sulfur, 0.80% mercaptan sulphur. Average temperature: 300° F. Duration of test 55 days.

Material	Corrosion Rate, Inch per Year	
Monel	0.0016	
Nickel	0.0016	
Inconel	0.0003	
Metal B	0.014	
Metal C	0.033	(e)

(e) Pitted to max. depth of 0.018 inch during test.



A good way to simplify the job of metal selection is to let the results of a Corrosion Spool Test guide you.

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The answer to your problem may be in their files now. But if it is isn't, INCO's CES will be glad to work with you in finding it. There's no charge, of course—and no obligation. A letter to "Corrosion Engineering Section" at the address below will bring you full details by return mail.

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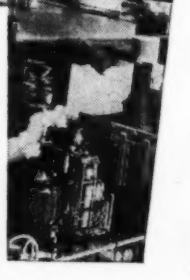

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MONEL...YOUR PARTNER IN PROGRESS

Patent Trends in Petroleum Refining

By PETER J. GAYLOR
Patent Attorney and Editor "The Technical Survey"

Reversible Greases

REVERSIBLE GREASES are those grease compositions which can be heated to above their melting point and, upon being cooled, revert to their original consistency. This type of lubricant has been adapted for use in "lubricated-for-life" bearings, and similar applications subjected at times to high temperatures. Electrical generators on Diesel locomotives employ such greases.

The preparation of a transparent grease of this type is disclosed in U. S. Patent 2,444,970 issued to Standard Oil Development Co. A steam-jacketed scraped-wall grease kettle was charged with 3000 grams of a 30% concentrate of calcium sulfonate (approximately 900 mol. wt.), and 3000 grams of a 65 viscosity at 210° F. naphthenic distillate oil was blended in by agitating at 180° F. to 200° F. When the solution was complete, 180 grams of calcium acetate as an 18.4 aqueous solution was added, emulsification taking place immediately. Five drops of an organic silicon polymer were added to control foaming and the temperature rapidly brought up to 250° F., a grease structure having started to develop at 230° F. Cold water was introduced into the jacket of the kettle and stirring continued until the grease had reached a temperature of 100° F. at which point it was removed and packaged. A clear, bright grease having the following characteristics was obtained.

Melting point.....In excess of 400° F.	
Penetration at 77° F.	242
Working penetration	278

The grease was quite resistant to breakdown through contact with water, as measured by directing a stream of water against a revolving frictionless bearing packed with the grease, and, in a pressure viscosimeter, no substantial change in consistency was noted between the temperatures of 190° F. and 350° F.

The plotted results of pressure-viscosity determinations in the range from 70° F. to 350° F. in several typical greases are shown in Fig. 1 wherein curve A shows the pressure in pounds per square inch developed in a pressure viscosimeter by the grease made in accordance with Example 1 of the specification. The values for curve B were obtained by testing a conventional soda base grease. Curve C represents a mixed soda lime base grease and curve D a lime soap grease. A line of demarcation is indicated in the drawing at 5 pounds per square inch pressure since it is probable that a grease having this low resistance to flow would tend to leak out of a small clearance under very slight stress.

It will be observed from the viscosimeter data curves that this type of grease (Curve A) is superior to a high temperature soda grease (Curve B) up to 300° F.

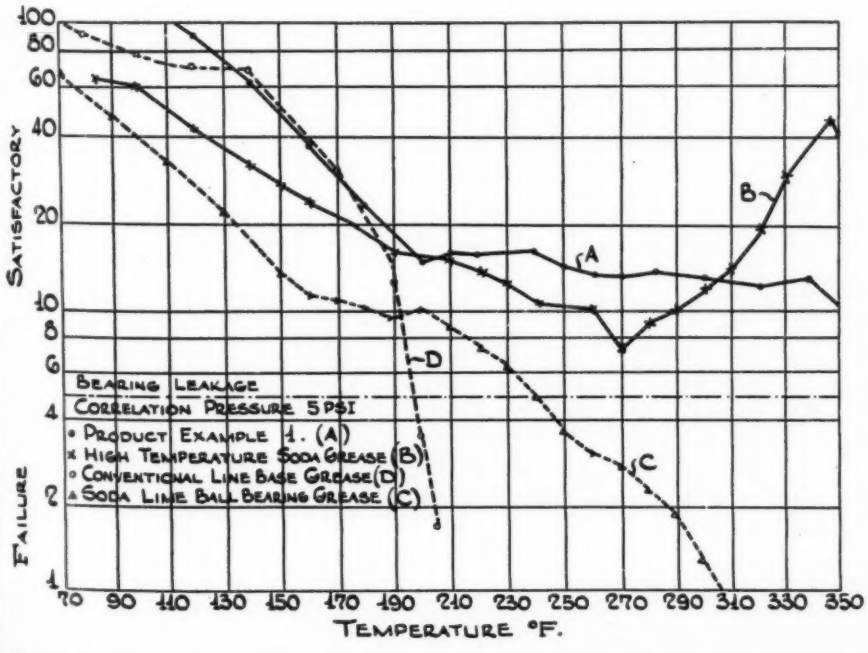

Fig. 1—Pressure viscosimeter data for various greases, including a transparent reversible grease (A) recently developed by Standard Oil Development Co. (U.S. Patent 2,444,970)

Swelling of Textile Fabrics

A BRITISH FIRM, Tootal Broadhurst Lee Co., Ltd., of Manchester, has found that textiles may be improved with respect to sheer appearance, hand, and stiffness by the use of "white spirit" in conjunction with other treating agents.

In one example (given in its U. S. Patent 2,445,064), plain bleached cotton fabric was steeped for one hour at room temperature in a solution consisting of 1 gm. of caustic soda, 40 cc. of butyl alcohol, and 460 cc. of "white spirit", and then mangled and immersed for 1 hr. in a 3% solution of carbon bisulfide in "white spirit". The fabric was then mangled and plunged into 10% aqueous sulfuric acid, followed by thorough washing and drying. The resulting fabric had increased stiffness and dyed more deeply with Chlorazol Sky Blue FF, as would be expected if the surface of each cotton fiber consisted of cellulose regenerated from cellulose xanthate.

The liquid reagent is said to have a flash point above 60° F. by the Abel test. "White spirit" boiling in the range 150-200° C. was employed.

Regulating Viscosity of Polymers

WORKERS AT CALIFORNIA Research Corp. have found that it is possible to regulate the viscosity of polymers obtained by polymerizing unsaturated hydrocarbons with boron fluoride catalyst.

In their U. S. Patents 2,442,644-5, these investigators disclose the addition of sulfur dioxide to the polymerization reaction in order to control the chain length of the polymer. Liquid sulfur dioxide forms coordinate compounds with boron fluoride ($BF_3 \cdot SO_2$). This compound is sufficiently unstable to dissociate at temperatures as low as −100° C, thereby releasing an adequate proportion of free boron fluoride catalyst mole-

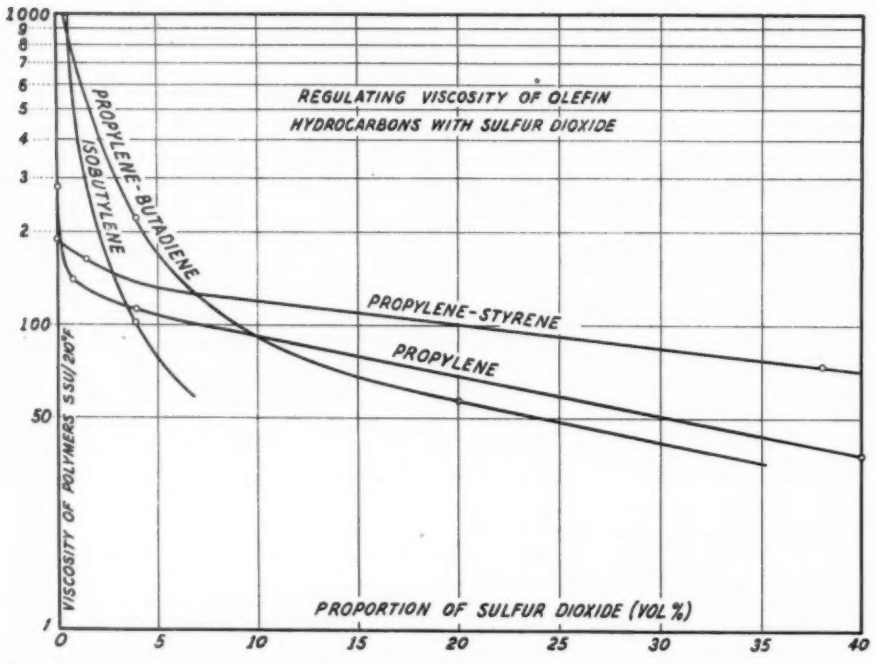

Fig. 2—Effect of sulfur dioxide in regulating the viscosity of olefin hydrocarbon polymers (California Research Corp., U.S. Patents 2,442,644-5)

cules to effect polymerization of the olefins. Also, liquid sulfur dioxide readily dissolves olefins, but loses its solvent power as the molecular weight increases. Hence, while lower olefins containing up to 5 carbon atoms readily dissolve in the liquid SO_2, higher olefins of over 10 carbon atoms are not soluble in this liquid and emerge as an oil phase above the solution. By this means it is possible to prepare narrow molecular weight range polymeric products.

In Fig. 2 are shown viscosity curves of olefin polymers produced in various proportions of sulfur dioxide present in the monomers prior to introduction of the boron fluoride. It has been found that in small amounts (below 1%), the action of sulfur dioxide is catalytic in that it activates the boron fluoride and increases the yield of polymer. In concentrations of 1-50% by volume, the chain transfer properties of sulfur dioxide become foremost. This chain-growth termination in the final polymerization step results in the shortening of the molecular chain and, consequently, in a lower molecular weight and a lower viscosity of polymer.

Selected Patents

U. S. PATENTS issued from July 21 to Aug. 17

U.S. 2,445,318 (Calif. Res.)—Magnetostrictive pickup unit.
U.S. 2,446,327-8 (Hydrocarbon Res.) — Fluidized conversion.
U.S. 2,445,345 (Union Oil)—Catalytic reforming.
U.S. 2,445,346 (SOD)—Titania-boria catalyst.
U.S. 2,445,351 (SOD)—Catalyst regeneration.
U.S. 2,445,360 (SOD) — Methylene cyclobutane aviation fuel.
U.S. 2,445,367 (SOD)—Stabilized diolefin.
U.S. 2,445,370 (SOD)—Catalytic cracking with activated clays.
U.S. 2,445,378-9 (SOD)—Alkoxypolyolefin polymers.
U.S. 2,445,520 (Socony)—Separating olefins.
U.S. 2,445,560 (Socony)—Alkylation.
U.S. 2,445,795-6 (Texas Co.) — Hydrogenation of carbon oxides.
U.S. 2,445,799 (Shell Dev.)—Polymers containing organic sulfur.
U.S. 2,445,874 (Phillips Petr.) — Radiation thermopile.
U.S. 2,445,935 (Shell Dev.)—Soda grease.
U.S. 2,445,936 (Shell Dev.) — Waterproof grease.
U.S. 2,445,983 (S.O. Ind.) — Sulfurizing terpenes.
U.S. 2,446,040 (Petrolite)—Desalting oils.
U.S. 2,446,076 (SOD)—Separating and purifying gases.
U.S. 2,446,100 (Socony) — Aluminum chloride catalysts.
U.S. 2,446,132 (Shell Dev.)—Silver catalysts.
U.S. 2,446,247 (S.O. Ind.)—Exothermic catalytic reactions.
U.S. 2,446,314 (Shell Dev.)—Polymers.
U.S. 2,446,426 (Hydrocarbon Research)—Synthesis of hydrocarbons with sulfur-containing catalyst.
U.S. 2,446,514 (Shell Dev.)—Separating aromatic hydrocarbons.
U.S. 2,446,536 (SOD) — Styrene - isobutylene films.
U.S. 2,446,547 (Houdry Process) — Conversion with Th phosphate catalyst.
U.S. 2,446,602 (Gulf Res.)—Destructive hydrogenation of heavy hydrocarbon oils.
U.S. 2,446,619 (Texas Co.)—Polymerization of olefins in presence of hydrogen.
U.S. 2,446,678 (S.O. Ind.)—Powdered catalyst conversion system.
U.S. 2,446,679 (Pan Amer. Refg.) — Refining toluene with sulfonic acid.
U.S. 2,446,783-4 (Socony) — Forming gel into beads.
U.S. 2,446,797 (Shell Dev.)—Catalytic oxidation of halogenated hydrocarbons.
U.S. 2,446,799 (Tide Water Assoc. Oil)—Absorbent refining.
U.S. 2,446,897 (SOD)—Polymerization.
U.S. 2,446,925 (SOD)—Cracking with suspended catalyst.
U.S. 2,446,927 (SOD)—Thickened lubricant.
U.S. 2,446,944 (Cities Service Oil)—High capillarity lubricating oil.
U.S. 2,446,947 (SOD)—Isobutene trimer.
U.S. 2,446,969 (SOD)—Inhibiting diolefin polymer growth.
U.S. 2,446,986 (Socony)—Apparatus for contacting gases with particle-form solids.
U.S. 2,446,998 (S.O. Ohio)—Catalytically treating hydrocarbons with HF and BF_3 in presence of H_2.
U.S. 2,447,016-7 (SOD) — Catalytic reforming and conversion.
U.S. 2,447,029 (USA)—Catalysts for benzene synthesis.
U.S. 2,447,043 (SOD)—Hydroforming.
U.S. 2,447,051 (Pure Oil)—Regenerating spent caustic.
U.S. 2,447,052 (Pure Oil)—Paint remover.
U.S. 2,447,117 (Universal Oil Prods.)—Vacuum stripping of moving catalyst.
U.S. 2,447,288 (Gulf Oil)—Amine salt of thiophosphoric acid.
U.S. 2,447,323 (Socony) — Oxygen absorbent media.
U.S. 2,447,404 (Calif. Res.)—Decolorizing petroleum resins.
U.S. 2,447,426 (Odberg)—Carbon monoxide.

FOREIGN PATENTS (and Applications)

Brit. Appl. 5370-5/48 (Shell)—Metal coating.
Brit. Appl. 5351/48 (SOD)—Lubricant.
Brit. Appl. 5352/48 (SOD)—Hydrocarbon polymers.
Brit. Appl. 5591/48 (SOD)—Hydrocarbon synthesis.
Brit. Appl. 5875/48 (SOD)—Motor fuels.
Brit. Appl. 6005/48 (SOD)—Oxidation of aromatic compounds.
Brit. Appl. 5762-3/48 (Texaco Dev.) — Radiation detecting devices.
Brit. Appl. 11380/48 (duPont) — Purifying hydrogen-rich gases.
Brit. Appl. 11799/48 (SOD)—Cyclo-alkadienes.
Brit. Appl. 14834/48 (Anglo-Iranian Oil) — Desulfurizing.
Brit. Appl. 14737/48 (Distillers Co.)—Hydrocarbon synthesis
Brit. Appl. 14869/48 (duPont)—Vapor phase reactions.
Brit. Appl. 15206/48 (SOD)—Hydrocarbon synthesis.
Brit. Appl. 14678-80/48 (Shell) — Dihydropyran derivatives.
Brit. Appl. 14681/48 (Shell)—Sulfurized products.
Brit. Appl. 14818/48 (Shell) — Synthetic lubricants.
Brit. Appl. 14936/48 (Shell)—Carbon monoxide.
Brit. Appl. 15038/48 (Shell) — Aqueous solutions.
Brit. Appl. 23129/47 (Shell) — Lubricating composition.
Brit. Appl 23482 & 24018/47 (Shell) — Synthetic lubricant.
Brit. Appl. 23720/47 (Shell)—Extreme pressure lubricant.
Brit. Appl. 1418/47 (Standard Oil Dev.)—Vapor-liquid contactor.
Brit. Appl. 14369/47 (SOD)—Chemical process.
Brit. Appl. 18717/47 (SOD) — Hydrocarbon Diesel fuels.
Brit. Appl. 4673/48 (SOD)—Olefins.
Brit. Appl. 5617/48 (Babcock & Wilcox) — Synthesis of carbon compounds.
Brit. Appl. 5370-5/48 (Shell)—Metal coating.
Brit. Appl. 5443/48 (Shell) — Fluid heating furnaces.
Brit. Appl. 5878/48 (Shell)—Esters.
Brit. Appl. 5879/48 (Shell)—Diamines.
Brit. Appl. 5351/48 (SOD)—Lubricant.
Brit. Appl. 5352/48 (SOD) — Hydrocarbon polymers.
Brit. Appl. 5591/48 (SOD)—Hydrocarbon synthesis.
Brit. Appl. 5875/48 (SOD)—Motor fuels.
Brit. Appl. 6005/48 (SOD)—Oxidation of aromatic compounds.
Brit. Appl. 3353-78 & 4248/48 (Anglamol)—Lubricants.
Brit. Appl. 22771/47 (Dow-Corning) — Antifoaming composition.
Can. 447,053 (Shell Dev.)—Mercaptan extraction.
Can. 447,054 (Sinclair Refg.)—Improving film strength of lubricants.
Can. 447,055 (Sinclair Refg.) — Decolorizing oil with clays.
Can. 447,056 (Sinclair Refg.)—Lube oil containing Ca salicylic ester.
Can. 447,060 (Union Oil)—Lube oil containing mixed soluble green and mahogany soaps.
Can. 447,066 (Dunstan et al)—Alkylated aviation fuel.
Can. 447,074 (Barrer) — Crystalline molecular sieve adsorbents.
Can. 447,601 (SOD)—Catalytic reaction.
Can. 447,602 (SOD)—Apparatus for short reaction time.
Can. 447,605 (Univ. Oil Prods.)—Alkylation.
Can. 447,606-7 (Univ. Oil Prods.)—Isomerization.
Can. 447,835 (Int. Lubricant Corp.)—Pb soap of hydroxystearic acid in grease.
Can. 447,852 (Shell Dev.)—Isomerization.
Can. 447,853 (Shell Dev.)—Cyclohexane from petroleum.
Can. 447,863 (Univ. Oil Prods.)—Isomerization-alkylation.

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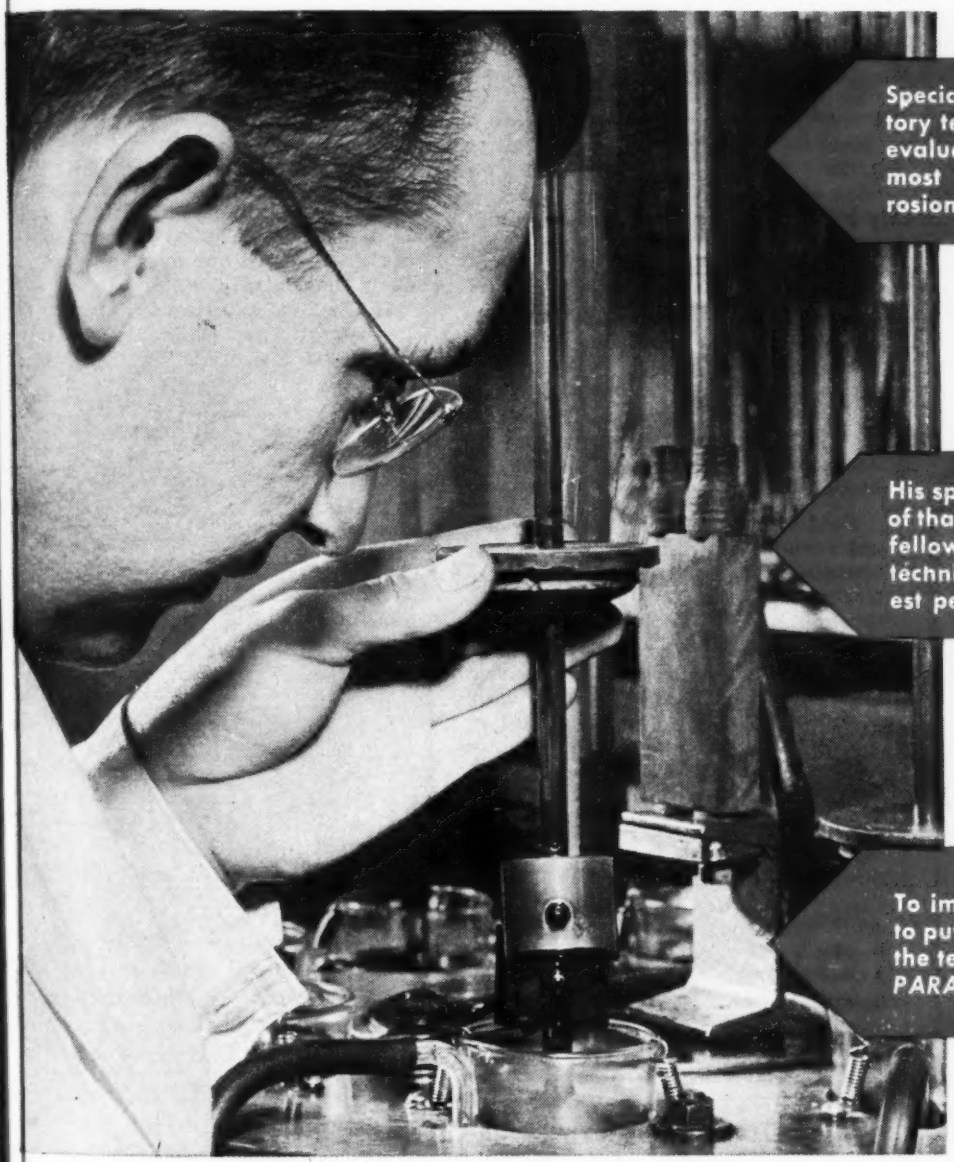

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Control Space Velocity in Reactor Using Telescoping Catalyst Pipes

In addition to the method for controlling space velocity described below, this month's review of new and improved devices used in petroleum processing and handling operations on which patents have recently been issued include:

- **Flame arrester cleaned quickly by combining with plug valve**
- **Thermocouple measures flow rates at low velocity**
- **Resilient gate makes storage tank gaging operation safe**

SPACE VELOCITY in a catalytic reaction vessel of the moving bed type can be controlled by a mechanical arrangement which provides for varying the height of the catalyst bed by use of feed pipes which can be set at various lengths.

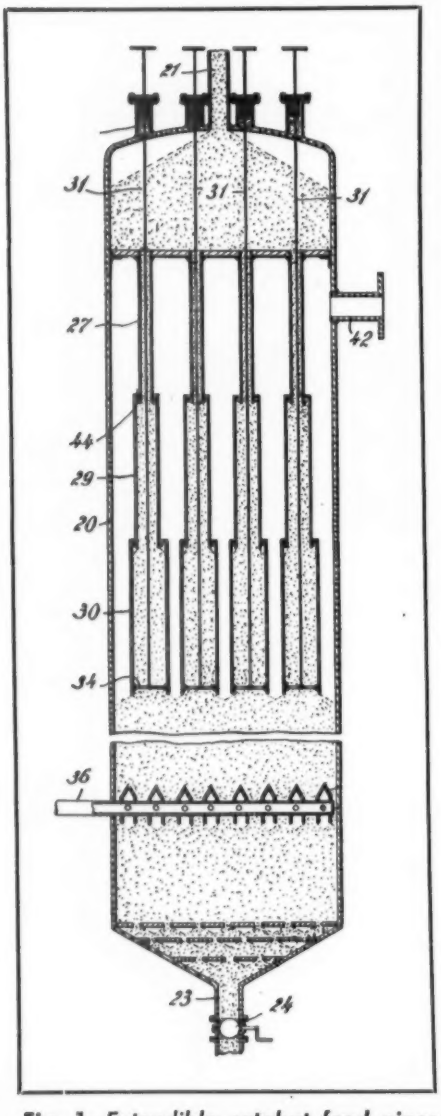


Fig. 1—Extendible catalyst feed pipes 27, 29 and 30 control height of bed in reactor (U. S. 2,446,986)

Because space velocity is an important variable and because such vessels operate most satisfactorily at relatively uniform loading, the oil throughput rate is held constant, and the control means are confined to varying the volume of contact mass material. For example, in a reactor of a given cross section, it is stated, space velocity may be doubled by cutting the height of the bed in half.

The device is shown in Fig. 1. Reactor 20 contains the conventional catalyst inlet 21 and outlet 23 with throttle valve 24; as well as reactant gases inlet 36 and outlet 42. Bed depth variations are accomplished by the telescoping feed pipes, 27, 29, 30. Any convenient control means may be attached to rods 31 for raising and lowering these extendible pipes. The catalyst bed height can be changed from the level represented by 44 to that at 34.

U. S. 2,446,986, issued August 10, 1948, to Thomas P. Simpson, assignor to Socony-Vacuum Oil Co., Inc., Paulsboro, N. J.

Flame Arrester Cleaned Quickly By Combining with Plug Valve

COMBINING A FLAME arrester and a plug valve as one integral unit makes possible quick cleaning of the flame arresting elements without removing the entire unit from the line. Use of multiple units; for example, two in parallel, permits the maintenance of flow through the line by keeping one arrester on stream while the other is cut out for cleaning purposes.

The device is illustrated in Figs. 2 and 3. The flame arrester proper comprises a stack of dimpled metal discs 35. (Dimples 36 are shown only in Fig. 3). Gases pass through from inlet 23 to outlet 24. The plug valve consists of a conical and cylindrical shell 21. It is rotated and locked in closed or open position by handle 65 and the corresponding conventional locking mechanism. It is in the open position in the drawings.

When it is necessary to take out the flame arrester plates for cleaning, the plug valve is turned to the closed position, and the bottom cover 15 of the unit is removed quickly and simply by the four handwheel nuts 17 on studs 18. The arrester assembly is then dropped out by removing nut 42 on the central bolt 41.

U. S. 2,447,120, issued August 17, 1948, to Richard C. Hall assignor to Petroleum Essentials, Inc., Glendora, Calif.

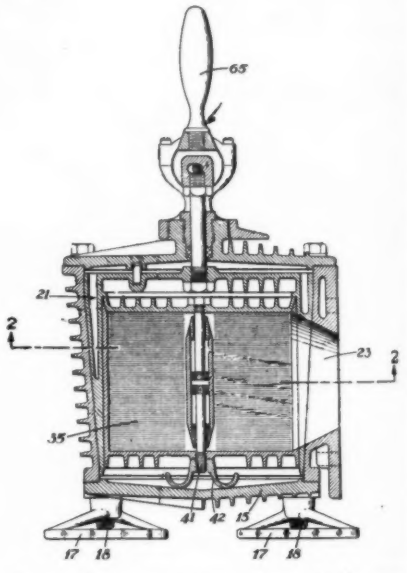


Fig. 2—Sectional view through the center of combination flame arrester and plug valve, on a bent plane indicated by the line 1-1 of Fig. 3 (U. S. 2,447,120)

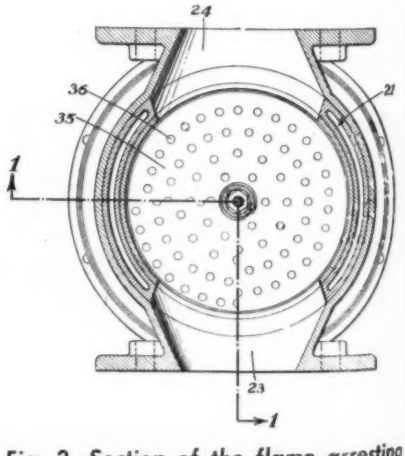


Fig. 3—Section of the flame arresting device on a plane represented by the line 2-2 of Fig. 2 (U. S. 2,447,120)

Measure Tank Contents Safely With Resilient Gaging Gate

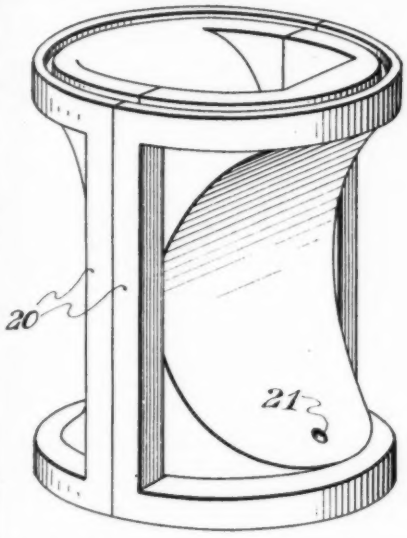


Fig. 4—Gager's plumb bob and line is inserted between resilient flaps 20 in this gaging gate (U. S. 2,446,577)

ESCAPE OF VAPORS and gases from an oil storage tank can be especially unpleasant and at times hazardous to the workman gaging the tank contents where he drops a plumb bob and line through an opening in the roof. This is said to be eliminated in the gaging gate in Fig. 4.

The unit in the drawing is designed to be inserted inside a conventional, cylindrical, capped opening in the tank roof. Inwardly curved segments 20 meet in a gas tight fit above the center of the opening. They are constructed of a resilient material, so the plumb bob and line can be passed between them. The segments are provided with a breather vent 21 to allow for ready expansion and contraction as the bob passes through.

U. S. 2,446,577, issued August 10, 1948, to Phillips B. Drane and Clarence D. Laidley, Tulsa, Okla.

Use Thermocouple in Flow Meter For Low Velocity, High Pressure

AN ELECTRIC FLOWMETER can be used for measurement of very small flow rates through small conduits, particularly those that are difficult to meter by other methods; for example, hydrogen and other light gases. It is said to be adaptable to gases or liquids at high pressure and low velocity; or for use with corrosive materials, without complex construction.

The device operates through the use of a cold thermocouple junction "C" and a hot junction "H" as illustrated in Fig. 5. Each point is connected through the millivoltmeter 4 to complete a thermoelectric circuit. The tubing at connection "H" is heated by a constant voltage coil to provide a hot junction in the circuit. The connections are made so that fluid flow is from the cold toward the hot junction.

To illustrate the operation; a case is assumed where the instrument is used to measure the flow rate of hydrogen at 1000 psi. through a small stainless steel tube at low velocity into a vessel in connection with a chemical conversion process. Wires 2 and 3 are constant in this case. The switch 10 is closed and heating coil 6 is allowed to bring the tube up to maximum temperature at "H". With a given flow rate, the hot junction is cooled, the fluid removing heat in proportion to its flow rate. The rate is read from the calibrated millivoltmeter.

U. S. 2,446,283, issued August 3, 1948, to Herbert A. Hulsberg, assignor to Universal Oil Products Co., Chicago, Ill.

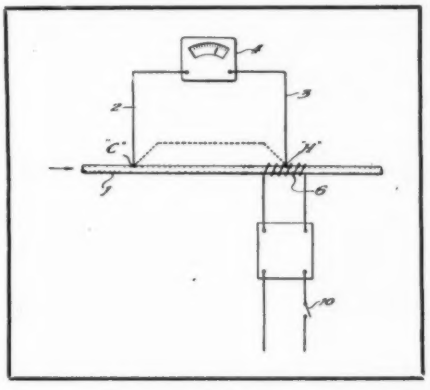


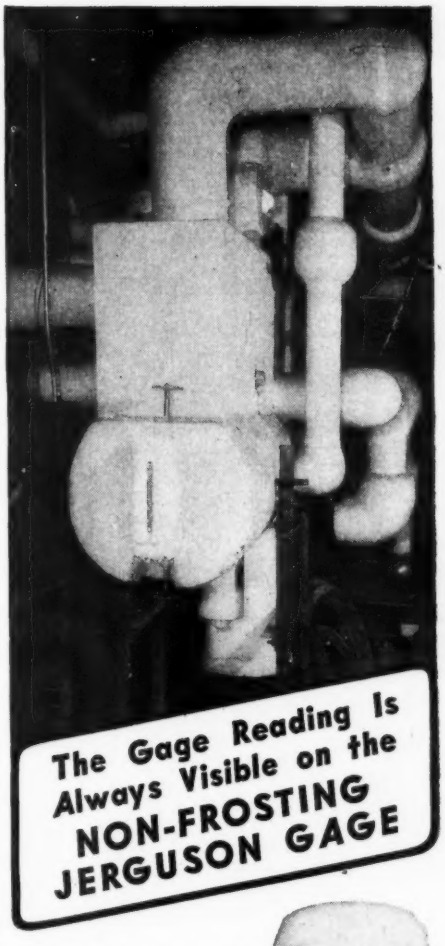
Fig. 5—Thermoelectric arrangement measures heat removed from point "H" by fluid in tube 1, in proportion to its flow rate (U. S. 2,446,283)

Other Recent Patents

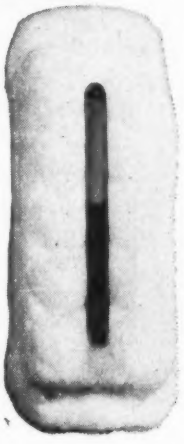
Space does not permit the complete review of all patents issued recently on equipment for the petroleum processing industry. Following, however, are brief abstracts of those with greatest interest:

Induced Draft Cooling Tower of multiple cell type is octagonal in cross section, so as to reduce inefficiencies from "dead air" spaces encountered in conventional square tower design. U. S. 2,445,908, issued July 27, 1948, to James G. De Flon and George W. Meyer, assignors to The Fluor Corp., Los Angeles, Calif.

Pulsation Dampener for removing pulsaltions from fluid streams from piston-type pumps, for example; utilizing a liquid seal between the pressure responsive diaphragm and the line liquid to protect the diaphragm material against corrosion or solvent ac-



Special design of the Jerguson Non-Frosting Gage prevents frost from forming over the vision slot.



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tion. U. S. 2,446,358, issued August 3, 1948, to Cecil F. Yates and Claude B. Nolte, assignors to the Fluor Corp., Los Angeles, Calif.

Lifting Sling Guide for erection of tall fractionating towers and the like, which can be inexpensively fabricated and welded permanently to the vessel and which is said to reduce wear on cable and provide the positive slip-proof grip needed. U. S. 2,443,307, issued June 15, 1948, to T. S. De Cuir, assignor to The Lummus Co., New York, N. Y.

Pipe Wrench using a reciprocating jaw similar to a small pinion gear with directional teeth to aid in getting a good "bite" on the pipe, and including a quick acting ratchet arrangement operated with one finger of the hand holding the wrench. U. S. 2,446,212, issued August 3, 1948, to Marion A. Clark, Tulare, Calif.

Reducing Flange for joining pipe of different sizes without requiring two extra flanges and a reducing fitting. U. S. 2,446,481, issued August 3, 1948, to Louis Letterman, Winthrop Mass.

Testing Device for condenser, heat exchanger, boiler, and similar tubing which provides for obtaining data on longitudinal tension stresses as well as data on circumferential tensile stresses, both types of information being obtained at the same time. U. S. 2,445,876, issued July 27, 1948, to Herbert S. Fullerton, assignor to the Baldwin Locomotive Works, Philadelphia, Pa.

Packing for pressure or vacuum pumps is said to provide more positive fluid seal, particularly when drive shaft is not rotating, and under low pressure conditions, in addition to lessening wear and abrasion on shaft. U. S. 2,447,663, issued August 24, 1948, to Frank E. Payne, assignor to The Crane Packing Co., Chicago, Ill.

Self-Tightening Wrench uses a cam-operated mechanism which clinches the jaws automatically around the object to be turned as the wrench is applied to the work. U. S. 2,441,144, issued May 11, 1948, to Roy L. Gregory, Everett, Wash.

How to Obtain Patents

Readers may obtain copies of any U. S. patents from the Patent Office at 25 cents each. Order by patent number from: The Commissioner of Patents, Washington 25, D. C.

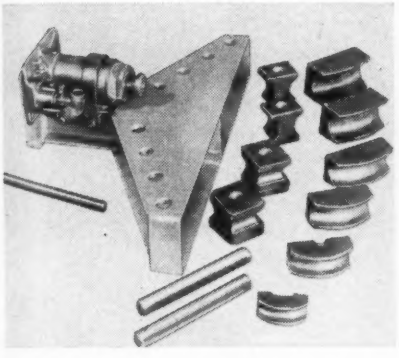
FOR MORE INFORMATION—use one of these reply cards to request additional details or literature on any items reviewed in "What's New!" Just circle the numbers corresponding to the items you're interested in, fill in the rest of the card, and drop it in the mail. No postage needed.

EQUIPMENT MATERIALS PROCESSES LITERATURE

What's New!

Reviewed by WILLIAM C. UHL, Equipment Editor

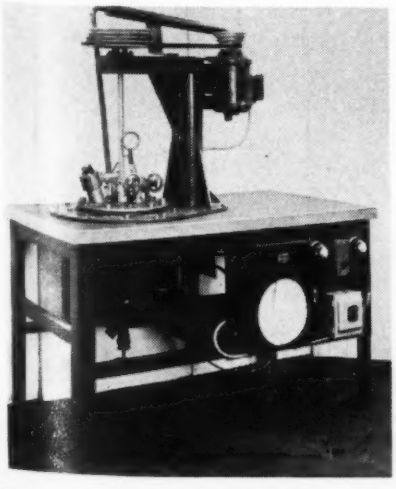
1—Pipe Bender



A lightweight, portable, pipe and conduit bender weighs 83 lbs., and features a removable hydraulic jack that can be used for other jobs. Unit is electrically welded construction and includes a set of dies for pipe of ¾, 1, 1¼, 2, and 2½ in. outside diameter. Electric Cord Co.

2—Pilot Plant

A new portable, five-gal., pilot plant, complete with instrumentation and working table, although designed primarily for research in resins, is applicable to other types of research. Kettle has a 2-in. charging opening but entire top cover assembly is removable. Discharge is through a 1-in. plug type valve in bottom head. The condenser is of the Liebig type with heat transfer area of 0.5 sq. ft. Internal equipment includes a 5-in. straight blade open turbine agitator and a helical coil for heating or cooling with steam or water. Jacket heat is applied by three electrical resistance heaters arranged in three circuits for use singly or in combination at various levels; each has a 2 kw. capacity. Variable speed of agitation is provided by a ½ hp. motor drive and step pulleys; speeds range from 443 to 869 ft./min. (peripheral). Allowable process pressures are from 15 psi. to full vacuum. Instrumentation includes indicating and recording temperature controller of on-off type, kettle pressure-vacuum gage, and other accessories. Blaw-Knox Co.

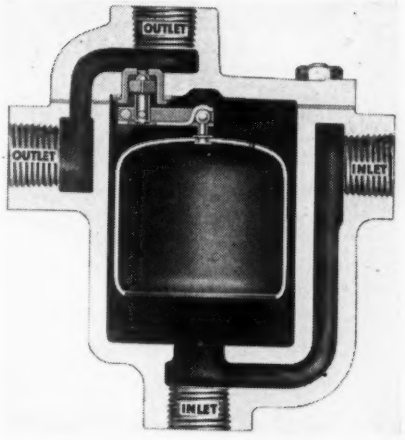


3—Glassware Cleaner

"Aquet," a new cleaning solution for laboratory glassware, is a solution of aromatic polyglycol ether which cuts away grease by preferential adhesion to the glass. Lowering of surface tension produces a high emulsion action. If water is used at 100° F., glassware will dry in two minutes on a rack, manufacturer states. Wiping and drying are not required. The material is nontoxic and non-sensitizing to the skin. It is recommended for all cases in which a wetting agent is required, and is said to be particularly adapted for cleaning burets to eliminate drainage errors. Emil Greiner Co.

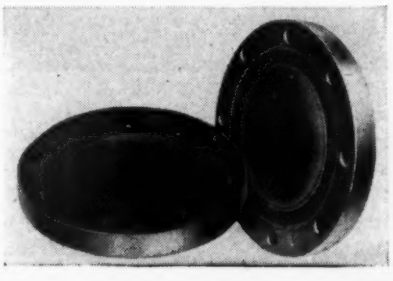
4—Steam Trap

Small size, versatility, and low cost are features of the Clark "60" inverted bucket type steam trap. Piping arrangement provides a choice of horizontal or vertical connections at either inlet or outlet, or a combination of both. The trap is furnished with various size orifices for working pressures up to 150 psi. and temperatures up to 375° F. Design of operating parts is same as for conventional larger traps. Clark Mfg. Co.



5—Safe Blind Flange

The "Gatke" Blind Flange line is suitable for moderate pressure operations where corrosive or flammable materials are handled. Non-metallic, the flanges are made of moulded fabric materials and are non-sparking when struck by metal, stone, or other similar materials. They have been tested at 400 psi. live pressure, and will withstand 15 to 20% sulfuric acid, it is reported. Sizes available are for 3, 4, 5, 6, and 8 in. pipe; other sizes can be furnished to specifications on quantity orders, the manufacturer states. Gatke Corp.



More "What's New!" Items, p. 1003

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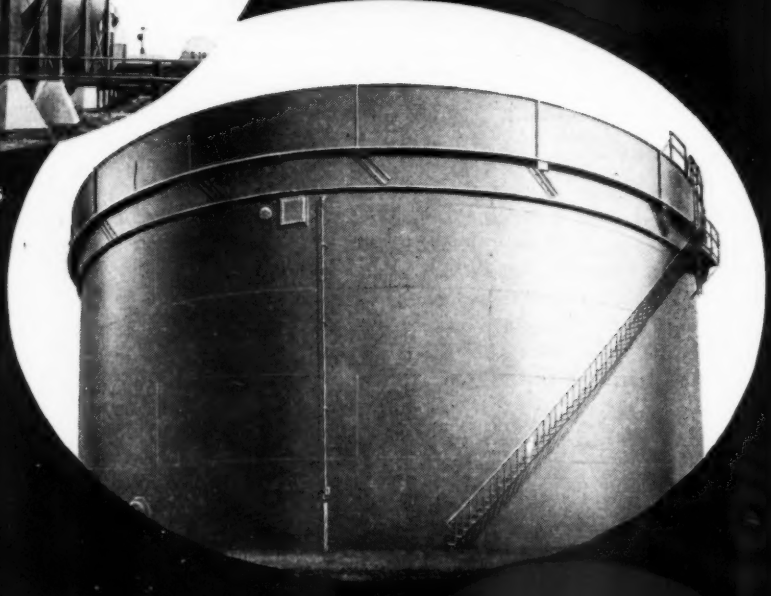

HAMMOND designs, fabricates and erects tanks of all types for liquid and dry storage . . . above or below ground . . . high or low pressure . . . cone roof . . . HAMMOND SPHERE . . . floating roof . . . VAPOR-LIFT . . . spheroid . . . GLOBE ROOF PRESSURE . . . gas holder . . . also stainless and stainless-clad vessels of all types and designs for the petro-chemical industries.

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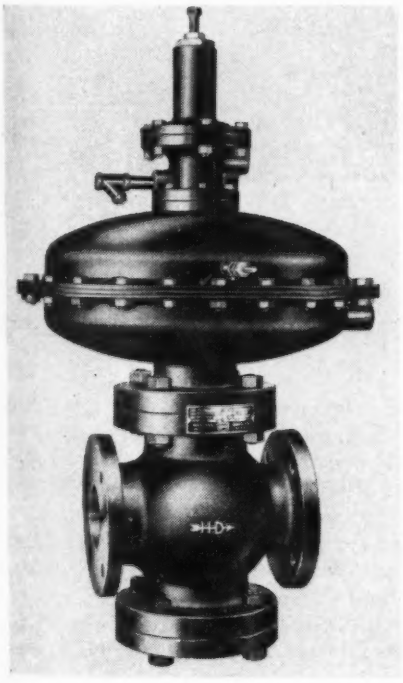
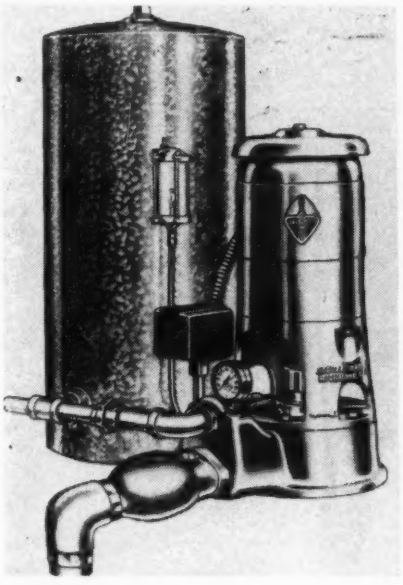
6—High Sensitivity Regulator

Improved sensitivity is said to be a feature of the new "5000 Series" Pressure Loaded Supersensitive Gas Regulator, available in sizes from ½ to 12-in. and maximum working pressure of 250 psi.; for air, gas, water, and oil service. Valves control pressure within a fraction of an inch water column with large variations in flow. They may be used on either reducing or back pressure service for any control pressure up to 100 psi. Body may be either cast iron or steel. Diaphragm cases are 3/16-in. steel stampings; the lower case is welded to a forged steel flange which is piloted into and bolted to the valve body, reducing height to a minimum. Standard trim material is Type 304 Stainless; other material available on request. Diaphragms are Neoprene with fabric insertion. Hammel-Dahl Co.



7—Self-priming Pump

The "Speedi-Prime" pump, designed for both shallow and deep wells to 40 ft., is said to be an adaptation of the Jacuzzi deep well injector pump for shallow well use. It is intended to solve the problem of border line cases—where the water level is sometimes too near the surface to justify a deep well pump installation and at other seasons where the water level lowers out of the range of the general run of shallow well units. Speed of priming test is 32 ft. in 4 minutes. Pump is offered



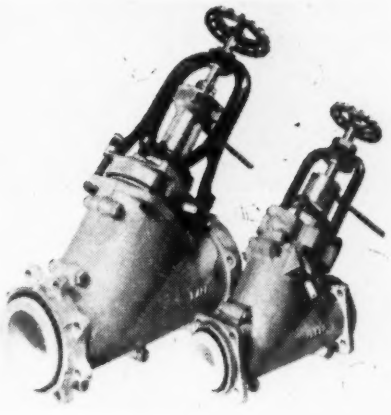
in wide horsepower and capacity range with choice of over-the-well or offset installation. Jacuzzi Bros. Inc.

8—Vacuum Tube Meter

The "Millivac" Model MV-17A, Vacuum Tube Millivolt Meter for DC operates on a different principle from other vacuum tube meters in that it has a magnetic modulator for converting the incoming DC signal into a 120-cycle wave which is then amplified, rectified, and metered. This is said to give the instrument complete stability with no drift and no zero adjustment except on its lowest range. It uses no bridge or differential circuit. It is designed for null detections in bridges, temperature measurements, RF thermocouple measurements, insulation leakages, etc. It reads 150 micro-micro amps, full scale; up to 10^{13} to 10^{14} ohms with an external voltage source; and operates on 115-volt, 60 cycles. Dimensions are 7 in. wide x 12 in. high x 6-in. deep. Millivac Instruments.

9—Armored Valves

A new line of armored porcelain valves are completely encased in an acid-resistant, aluminum shell. The body, plug, retaining rings—all parts with which corrosive materials can come in contact—are of solid, nonporous porcelain. The addition of the armor provides protection against breakage. Y valves are available in sizes 1-1/2, 2, 3, 4, and 6-in.; angle valves in 1 and 2-in.; flush valves in 1-1/2, 2, and 3-in. sizes for 3, 4, and 5-in. tank outlets. Lapp Insulator Co., Process Equipment Division.

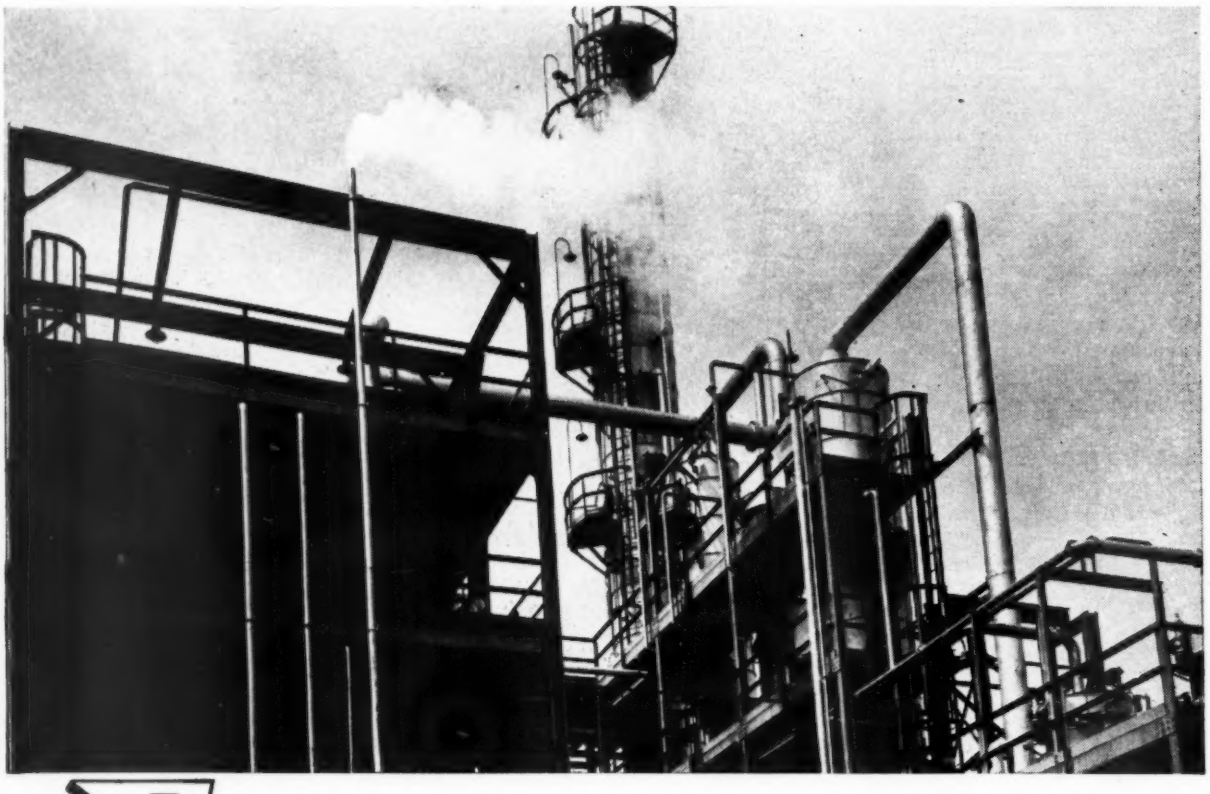


10—High Temperature Plastic

"Kel-F", a new plastic material, is said to have satisfactory properties over a wide temperature range, from −320° F. to +390° F., making it suitable for use at medium temperatures as well as in low temperature chemical reactions. Coupled with its resistance to corrosion, it is applicable for use as a substitute for glass in gages, flowmeters, instrument tubing, and the like. It is also said to have low "cold flow"; that is, it has good resilience, making it adaptable as seating material for air or gas pressure release valves which are closed for long periods of time. The material is also a good heat and electrical insulator, has high water resistance, and is readily fabricated. Chemically, it is a polymer of trifluorochloroethylene. M. W. Kellogg Co.

More "What's New!" Items, p. 1005

Something new under the SUNOCO emblem!



Furfural used in new Marcus Hook refinery

Sun Oil Company now joins the ranks of those refiners who have selected furfural for the solvent refining of lubricating oil. A new furfural solvent refining plant has just gone "on stream" at Marcus Hook, Pa., and is daily turning out 1800 bbls. of quality lubricants at low cost. Sun Oil selected the furfural process after thorough study and extended test. Their decision lends still further confirmation to the assurance of obtaining high yields of premium quality products by the furfural process applied to hydrocarbon oils.

Furfural in other industries and for other uses

The selective solvent properties of furfural which the oil industry has so widely recognized, are also being used in the refining of wood rosin, and the processing of glyceride oils, as well as in the extractive distillation of C_4 hydro carbons such as butadiene.

If you have a problem involving selective extraction, separation or refining, it may be that furfural can help you.

Furfural is also widely used in the manufacture of synthetic resins and in abrasive wheel manufacture.

And if you are interested in organic synthesis you should investigate furfural's chemical properties. This versatile aldehyde is fast assuming the same importance as an intermediate that it has as a selective solvent.

A request on your company letterhead will bring you a copy of Quaker Oats Bulletin 204—Current Uses of Furfural.

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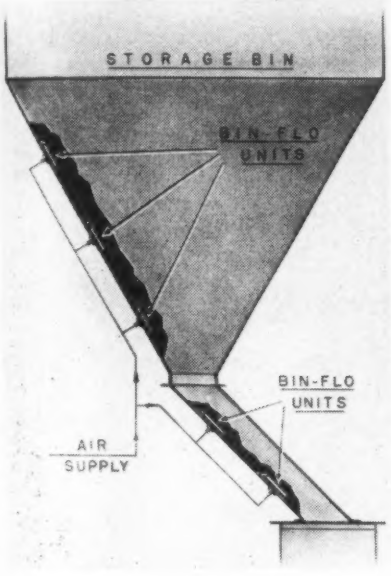
In Australia, Swift & Company, Pty. Ltd., Sydney
In Europe Quaker Oats-Graanproducten N. V., Rotterdam, The Netherlands; Quaker Oats (France) S. A. 42, Rue Pasquier Paris 8E, France

11—Material Flow

"Bin-Flo" is a new aerating device designed to provide uniform and steady flow of bulk materials from bins, hoppers, and chutes. The Bin-Flow unit is a small plate, 3-3/4 x 7-1/2 x 1/2-in. thick, which is located at points where flow is restricted and causing stoppages. Low pressure air is injected through a fabric diffuser, causing the material to flow freely. Manufacturer states the units will not plug up with dry, finely ground materials. Models are provided for various shaped bins and chutes. Piping can be run either outside of thin-walled bin or inside of thick-walled container. Bin-Dicator Co.

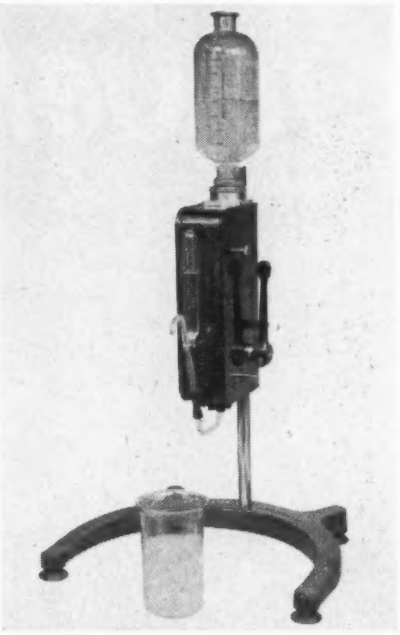


12—New Foam Liquid

National "99" is a new foam-type recharge, said to be the first produced for hand extinguishers suitable for fighting petroleum product, alcohol, and other polar organic fires. It may be used in any 2½ gal. foam type extinguisher and was developed particularly for chemical and other industries in which polar organic solvents are used because ordinary foam is not stable in such solvents. National Foam System, Inc.

13—Solution Dispenser

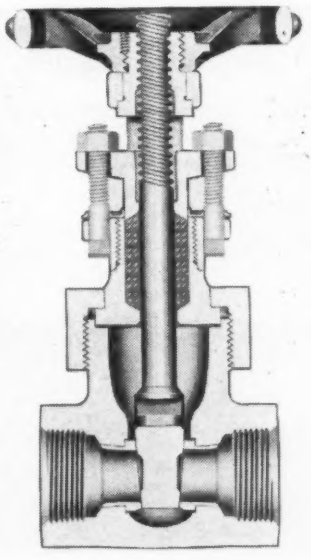
Accurate measurement and deliveries of solutions used in routine analyses up to 100 ml. can be made in the new "Precision" Solution Dispenser, and are said to be free from contamination. Reservoir is of Pyrex glass; liquids are sealed from the atmosphere, so that volatile liquids can be measured. Unit is designed for 100



ml. quantities, but may be varied by using other pipets to deliver 5, 10, 25, and 50 ml. Overall dimensions are approximately 32 in. high, 10 in. wide, and 13 in. deep. Precision Scientific Co.

14—Gate Valves

A new line of Crane, union bonnet, 600-lb., cast steel, gate valves, Nos. 3602XW and 3602X will replace Nos. 3606XW and 3606X. They are available in sizes 1/4 through 2 in., with screwed ends, and with two kinds of trim. The XW valves have Excelloy seats and a hardened stainless-steel disc. They are recommended for superheated or saturated steam, hot or cold water, ordinary air, natural gas, fuel oil, gasoline, butane, propane, and for fluids that are non-lubricating and relatively non-corrosive; top temperatures are 850° F. The X valves have both seats and disc of Excelloy and are for oil and oil vapors at temperatures up to 1000° F. They are not recommended for steam or other non-lubricating fluids, because the alloy seating faces have a tendency to gall in such service, particularly under high seating loads. Crane Co.



Trade Literature

15—Fire Extinguishers

Ansul Catalog, Form No. 4845, lists complete line of dry chemical type fire extinguishers and includes charts showing the characteristics of approved hand extinguishers and comparative effectiveness of various kinds on flammable liquid fires. Ansul Chemical Co.

16—Arc Welders

D-C Arc Welders, Bulletin GEA-4852, describes the WD-40 series of machines for 200, 300, and 400 amp. service. Includes dimensions, specifications, and wiring data. General Electric Co.

17—"Pancake" Motor

Axial Air Gap Motor, Bulletin 2760, provides specifications, applications, and features of construction of the new line of electric motors which are about half the size of conventional motors and weigh about 30% less. Fairbanks-Morse & Co.

18—Hydraulic Oils

The Fundamentals of Hydromechanics and their Relation to Hydraulic Oils, Panorama of Lubrication; Vol. I, No. 10; a 32-page booklet explaining the hydraulic behavior of liquids and how oil-using hydraulic machines and equipment operate. Shell Oil Co., Inc.

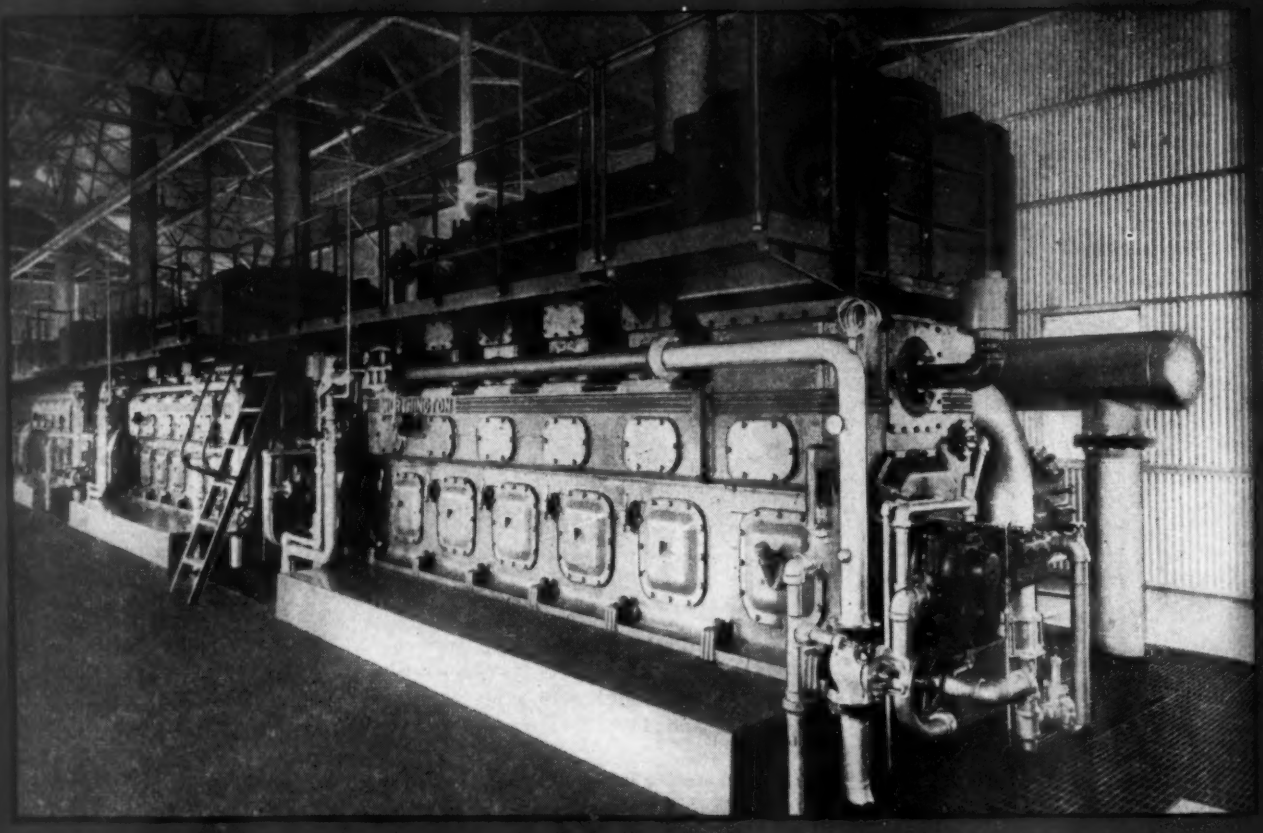
19—Position Control

L & N Electric Control, Position-Adjusting Type, a revised 40-page catalog outlines the many ways automatic controls are of help in any process involving valves, vanes, or dampers for regulating temperature, pH, conductivity, gas analysis, and the like in various industries; covering both Micromax line and Speedomax line for applications where unusual sensitivity and response speed are required. Leeds & Northrup Co.

More "What's New!" Items, p. 1008

Easier to Get At!...

WORTHINGTON ANGLE ENGINE COMPRESSORS



A Battery of Worthington Angle Gas Engine Compressors — Type LTC, 600 hp — in the Halliday, Texas, Plant of Warren Petroleum Company

In these views of Worthington LTC Angle Engine Compressors, note the size and number of covers on both main and compressor frames.

Thanks to this greatly increased accessibility, the work of maintenance crews is so simplified that keeping efficiency at peak is reduced to an easy, effortless routine.

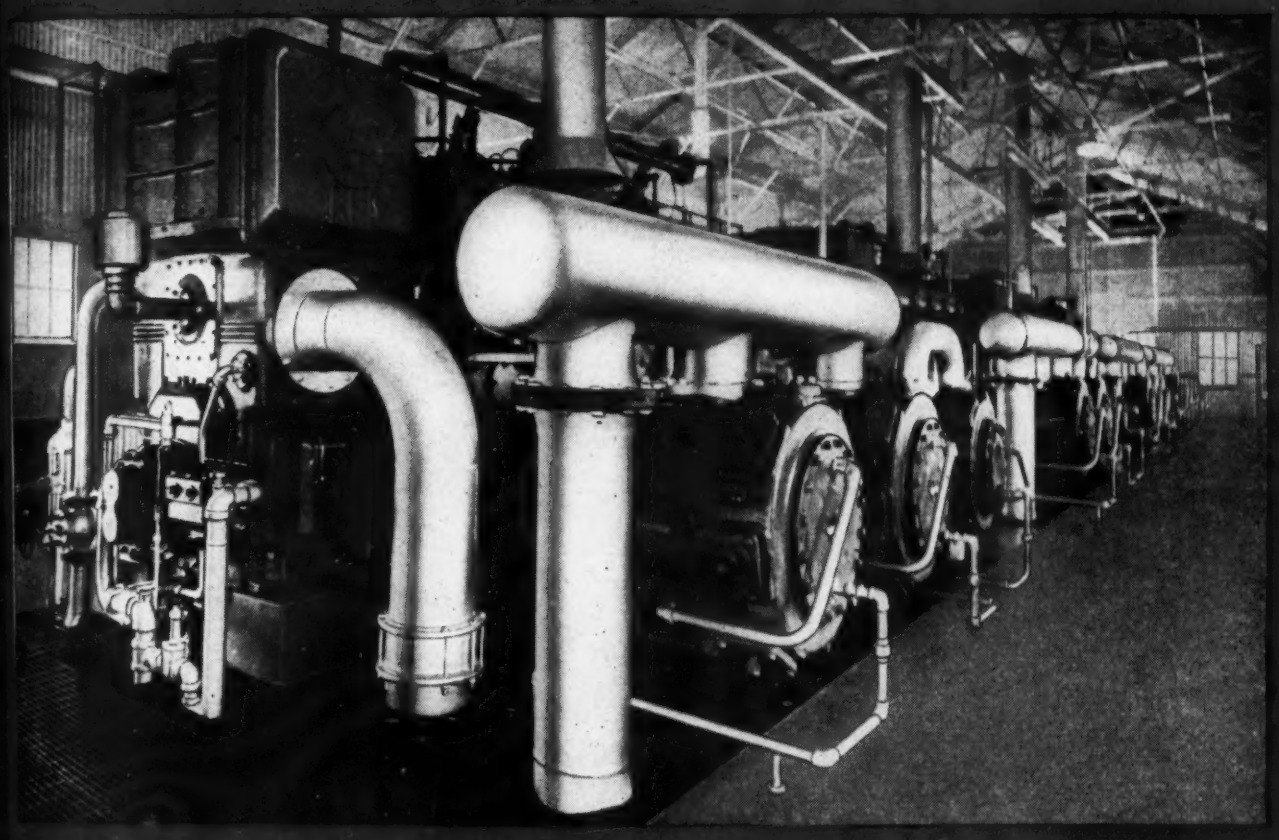
For proof, there's the fact that 99½% running time — day after day, year in and year out — is standard for LTC performance the world over.

And here's another fact: Continuous, record-breaking dependability like this

VERSATILE! Worthington LTC Gas Engine Compressors have been developed to meet many exacting requirements of the oil and gas industries. In pipe line service, for example, their outstanding ability to carry full loads "around the clock" assures economical, uninterrupted gas-transmission.

Easier to Keep Going!

FEATURE ACCESSIBILITY AND DEPENDABILITY



Another View of the Warren Petroleum Company Installation. Worthington Compressors of this Type Range from 400 to 1000 hp, in Four Sizes of Cylinder Combinations

makes big production gains a certainty.

Get the whole LTC story. Write for Bulletin L-690-B1 that shows you why *there's more worth in Worthington. Worthington Pump and Machinery Corporation, Compressor Division, Buffalo, New York.*

WORTHINGTON

EK8.3

NO OTHER COMPRESSOR WILL OUTPERFORM A WORTHINGTON

20—Valve Packing

EValpak, Catalog 12, Section R; gives sizes, specifications, and list prices on a line of heat-resisting, molded valve packing for valves from ¼ to 14-in. Edward Valves, Inc.

21—Pressure Gages

Hays Force Gage, Bulletin 48-888; an 8-page booklet describing gages for absolute and differential pressure, and for flow and liquid level. The Hays Corp.

22—Orifice Information

Capacity Data for Concentric Orifices and Flow Nozzles, Bulletin T-100-M; 10 pages of formulas and graphs giving a method for approximating the orifice or nozzle throat to pipe diameter ratios required for satisfactory fluid meter installations. Hagan Corp.

23—Air Filters

Staynew Intake Filters, Bulletin SIF, describes a line of air filters for internal combustion engines, compressors, blowers, motors, and generators; includes specifications and shipping weights. Dollinger Corp.

24—Soot Remover

Chemical Removal of Soot and Slag from Boiler Furnaces; a 12-page illustrated abstract of progress reports on soot removal research on Nalco SR-150, which removes coal soot by lowering its ignition temperature to 775° F., where normal furnace temperatures will burn it off. National Aluminate Corp.

25—Remote Controls

Hydraulic Remote Control, Bulletin 2001, an 8-page booklet giving descriptions and specifications of a line of units for control of valves, throttles, governors, pumps, winches, and the like. Sperry Products, Inc.

26—Vacuum Distillation

Vacuum Distillation of Petroleum Residues, a 13-page reprint of an article under the same title by W. W. Kraft, and appearing originally in *Industrial and Engineering Chemistry,* May, 1948. The author covers performance requirements, and describes engineering and process studies involved in designing equipment for this type operation. The Lummus Co.

27—Vinylite Plastics

Vinylite Resins and Plastics, Bulletin J-547a, 40 pages describing this line of plastic compounds, and including seven tables of average properties of the material in form of sheeting, film, rigid sheets, resins, and molding and extrusion compounds. Bakelite Corp.

28—Thermometers

Herco, Bulletin No. 208; a four-page folder covering catalog descriptions and prices of a complete line of etched scale and A.S.T.M. etched scale thermometers. Wm. Hiergesell & Sons.

29—Boiler Walls

Reintjes Floating Walls, Bulletin 748; presents in textual and illustrated form, a questions and answers forum on most frequent problems met in designing air tight refractory enclosures for water walled boilers. Geo. P. Reintjes Co.

30—Drafting Equipment

Emmert Drafting Machines, Bulletins 6-48 and 7-48, describe a new line of stainless steel drafting machines and equipment for sizes from 24 to 132 in. in height and any length, and for installation on any make board. Emmert Mfg. Co.

31—Cat Cracker Operation

Instrumentation, Vol. 3, No. 4; contains article by Sun Oil Co. chief instrument engineer on how narrow range control improved operation of Houdry catalytic cracking unit at Marcus Hook. Brown Instrument Co.

32—Tube Expanders

Airetool Tube Expanders, Bulletin No. 43; covers a line of tools for rolling and expanding boiler and heat exchanger tubes, and includes some short rules for care and maintenance of expanders. Airetool Mfg. Co.

33—Absorption Efficiency

Straight Line Chart Determination of Absorber Extraction Efficiency; a 32-page reprint of a paper under the same title by E. G. Ragatz, and presented before a joint meeting of the Southern California section of the American Institute of Chemical Engineers and the California Natural Gasoline Assn. Includes graphs, charts, etc., and work data sheets perforated for removal. Clark Bros. Co., Inc.

More "What's New!" Items, p. 1009

ERIE, for many years, has maintained high standards by stressing quality in the manufacture of special bolts and studs, a large portion of which are used by the oil refining industries in the manufacture of regular and high octane gasoline.
It will pay you to send us your inquiries which will be given our best attention.
ERIE BOLT & NUT CO.
ERIE, PA.
A SUBSIDIARY OF
Barium
STEEL CORPORATION
Steelwright to the Nation
STUDS • BOLTS • NUTS ALLOYS • STAINLESS • CARBON • BRONZE

350,000 bbls / day

new crude running capacity

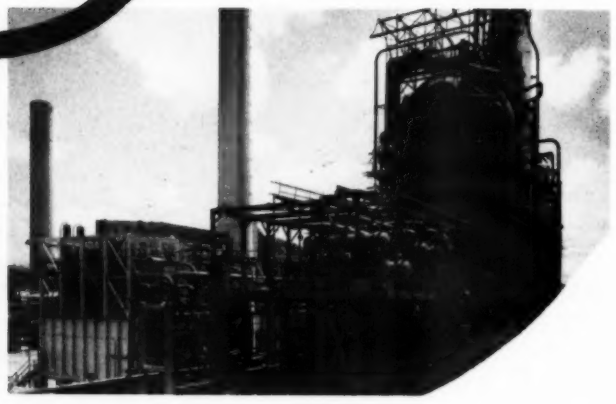
now being built by the Foster Wheeler Corporation ...18 multi-stage crude units, varying in size from 1,000 to 63,000 bbls/day in the United States... Venezuela... Brazil... Bolivia... Uruguay... Spain ... France... Burma. Many are for duplicates of FW units now in operation.

FOSTER WHEELER CORPORATION

165 BROADWAY, NEW YORK 6, NEW YORK

"THE BEST IS THE LEAST EXPENSIVE"

5 crude distillation units for one refiner



5 new crude distillation units, with a total daily capacity of 139,000 barrels, representing the combined experience of the engineering departments of The Texas Company and the Foster Wheeler Corporation.

Design of all these units follows, essentially, that of an original successful pattern—a 40,000 bbls/day unit built in 1943.

Successful patterns save time—and money.

FOSTER WHEELER CORPORATION

165 BROADWAY, NEW YORK 6, NEW YORK

What's New!

34—Power Tools

Portable Power Tools, Catalog No. 486; illustrates and describes portable power driven hammers, vibrators, drills, grinders, sanders, etc., including suggestions for proper use. Syntron Co.

35—Condensate Return

CBA Condensate Booster System, Publication 3250-1; gives specifications, and dimensioned drawings on line of high differential, high pressure, condensate return systems in six sizes from 3 to 25 hp., based on a maximum of 200 psi. pressure differential. Cochrane Corp.

36—Boiler Blow-off

Everlasting Valves, Bulletin E-120, lists a blow-off valve line in quick-reference arrangement for selecting valves for requirements of pressure, operating method, and ASME codes; including complete dimensions. Everlasting Valve Co.

37—Stainless Steels

Tempil Topics, Vol. 3, No. 9; is a data sheet on the composition and properties of martensitic and ferritic stainless steels, and comparing them with carbon steel, nickel, copper, aluminum, magnesium, and beryllium. The Tempil Corp.

38—National Standards

ASA Price List, No. 4801, March, 1948, provides an up-to-date price list of all national standards approved by the American Standards Association.

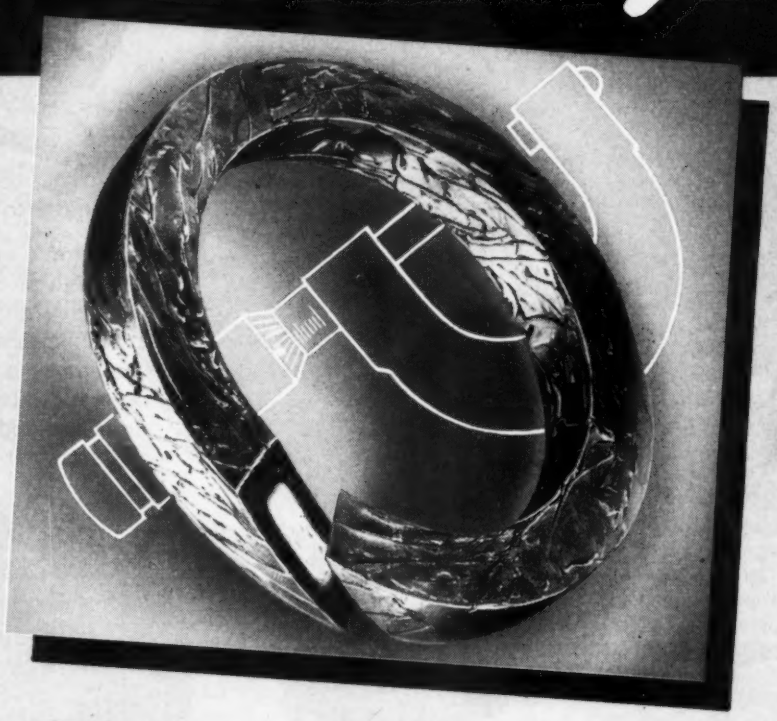
39—Laboratory Instruments

Aminco Scientific Instruments, Catalog 48; a 273-page catalog, indexed and illustrated, on a complete line of instruments for research and testing laboratories. American Instrument Co.

For Your Convenience

Business reply cards are included in this issue of PETROLEUM PROCESSING to assist you in obtaining more information on any items reviewed in "What's New!" You'll find them facing page 1001. Just circle the numbers corresponding to the numbers on the items you're interested in, fill in the bottom of the card, and drop it in the mail. No postage required.

DURAMETALLIC Packings



PRECISION made die-molded packing rings by Durametallic present 3 points of sealing satisfaction:

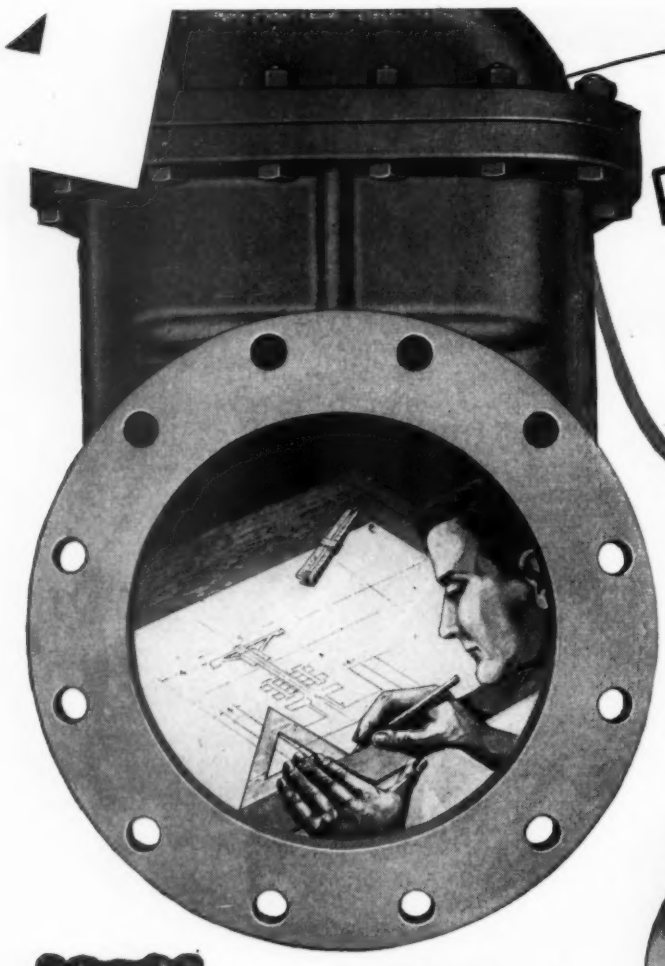
1. They provide a perfect fit for your stuffing box.
2. They save time, labor and eliminate waste.
3. They are tailor-made to insure a more accurate packing installation.

WRITE TODAY FOR FILE DMPP . . . containing illustrated bulletins on Durametallic Packings—with specifications and data toward answering your sealing problems

The PERFECT SEAL

DURAMETALLIC CORPORATION
KALAMAZOO MICHIGAN

MANUFACTURERS OF METALLIC and SEMI-METALLIC PACKINGS
ROTARY MECHANICAL SEALS and PACKING TOOLS



There's Precision Engineering in every POWELL VALVE

Powell makes valves by the thousands. We have to in order to satisfy the nation-wide demand.

But don't be misled! We know that quality often suffers through so-called "mass production" methods. So every Powell Valve from a standard small bronze globe to the most special design for corrosion resistance is given the most meticulous, individual attention. That's why Powell Valves have such an outstanding reputation for long life and dependable performance in every branch of industry. It pays to install Powell Valves.

Fig. 1561—Class 150-pound Cast Steel Swing Check Valve with flanged ends and bolted cap. Disc has ample lift to permit full straightway unobstructed flow through the valve body.

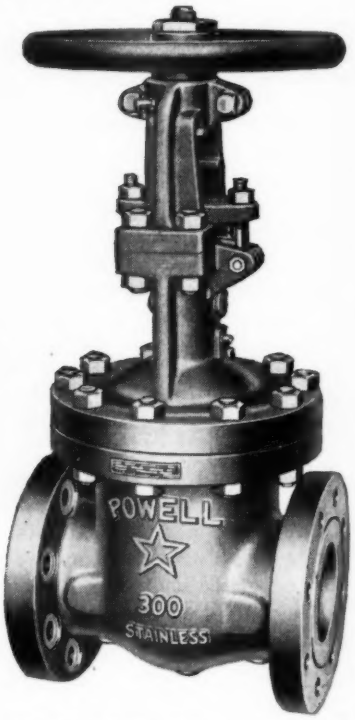


Fig. 3003 S. S.—Class 300-pound Stainless Steel Gate Valve with outside screw rising stem, bolted flanged yoke and tapered solid wedge.

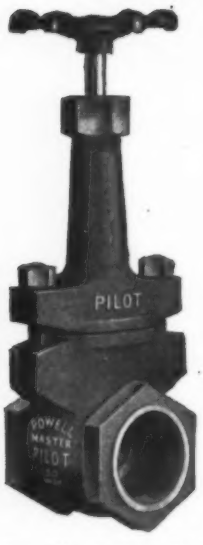


Fig. 1460—Iron Body Bronze Mounted "Master Pilot" Gate Valve, with screw ends, rising stem, bolted flanged bonnet and tapered solid wedge.

Fig. 514—150-pound Bronze Gate Valve with screwed ends, screwed-in bonnet, inside screw rising stem and tapered wedge, solid or double.

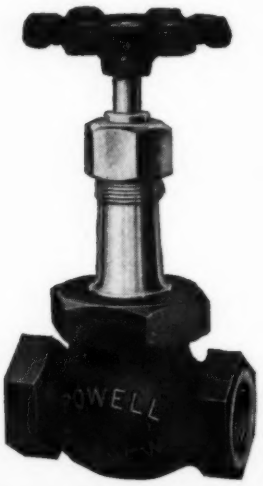


Fig. 190—150-pound Iron Body Bronze Mounted "Irenew" Globe Valve. Has screwed ends, union bonnet and regrindable, renewable, wear-resisting "Powellium" nickel-bronze seat and disc.

The Wm. Powell Co., Cincinnati 22, Ohio

DISTRIBUTORS AND STOCKS IN ALL PRINCIPAL CITIES

POWELL VALVES

Hydrogen and Synthesis Gas Production

By R. M. REED and ARNE ERIKSEN

The Girdler Corp., Louisville, Ky.

Present-day status of the hydrocarbon-steam process for the manufacture of hydrogen and mixtures of hydrogen and other gases for various purposes, from natural gas, light hydrocarbons and steam, is reviewed.* While the process was originally applied for the hydrogenation of various petroleum materials, it was used on a large scale during the war in the synthesis of ammonia and has also found various applications in the chemical and food industries. It has also been found adaptable for the production of gas mixtures suitable for supplementing manufactured gas. The process has been adapted for the use of propane and butane as process materials, so that hydrogen plants can be built where natural or refinery gas, the original feed materials, are not available.

THE hydrocarbon-steam process for the production of hydrogen and various mixtures containing carbon monoxide and hydrogen has become increasingly important in recent years. A brief description of this process together with typical applications of its current use in various fields is presented here.

Hydrocarbons will react with steam over catalysts at elevated temperatures so that the hydrocarbons are almost completely converted to carbon oxides and hydrogen. The two principal reactions which occur with the paraffin hydrocarbons are:

$$C_nH(2n+2)+nH_2O=nCO+(2n+1)H_2 \quad \ldots\ldots (1)$$

$$C_nH_{(2n+2)}+2nH_2O=nCO_2+(3n+1)H_2 \quad \ldots\ldots (2)$$

These reactions are both endothermic. Reaction 2 is considered to be the summation of reaction 1 and:

$$nCO+nH_2O=nCO_2+nH_2 \quad \ldots\ldots (3)$$

Hydrogen for Petroleum Hydrogenation

Although the patent literature in connection with this process dates back to about 1880, the first large-scale commercial development was for the purpose of producing relatively pure hydrogen, and was carried out by the Standard Oil Co. of New Jersey through its development company working jointly with I. G. Farbenindustrie. A large plant was installed at Bayway, N. J. in 1930 and a second and larger plant was placed in operation in 1931 at Baton Rouge, La.

In this latter plant, natural gas was reacted with steam to produce a mixture of carbon monoxide, carbon dioxide and hydrogen at about 1600° F., in a furnace containing vertical chrome-nickel alloy steel tubes. The furnace tubes contained a nickel catalyst supported on a refractory material. The hydrocarbon-steam reaction occurred as the natural gas and steam were passed down through the tubes. On the outlet of the furnace, the gaseous products were cooled by the addition of more steam, and the mixture was then passed through a catalytic converter containing an iron oxide catalyst which promoted the oxidation of carbon monoxide to carbon dioxide (reaction 3 above). This reaction took place at about 850° F.

The gas mixture from the catalytic converter was cooled and stored in a gas holder. The gas contained about 77% hydrogen with about 18% carbon dioxide and the balance carbon monoxide, methane and nitrogen. On removing the carbon dioxide from this gas mixture by scrubbing with monoethanolamine solution (the Girbotol process), a hydrogen gas was obtained which contained about 95% hydrogen together with roughly 1.5% methane, 2.0% carbon monoxide, 1.5% nitrogen (present originally in the natural gas), and a trace of carbon dioxide.

This gas was suitable for the hydrogenation of various petroleum materials and has been used off and on for this purpose on a large scale since 1931, particularly during the war. Several other rather large plants have also been installed since 1931 for the production of hydrogen for the hydrogenation of petroleum products, namely at Port Arthur, Texas; Whiting, Ind.; Salt Lake City; Richmond, Cal.; and Aruba, N. W. I., but some of these have discontinued operation as a result of the development of more economical processes for producing all grades of gasoline.

Hydrogen for Ammonia Synthesis

The second large-scale utilization of the hydrocarbon-steam process for the production of hydrogen-containing gas mixtures has been in the field of ammonia synthesis. This process has been employed on a large scale in the following synthetic ammonia plants: Hercules Powder Co. at Hercules, Cal., and Louisiana, Mo. (Missouri Ordnance Works); Alberta Nitrogen Products Ltd. at Calgary, Alberta; Spencer Chemical Co., Pittsburg, Kan. (Jayhawk Ordnance Works); Lion Oil Refining Co., El Dorado, Ark. (Ozark Ordnance Works); Commercial Solvents Co., Sterlington, La., (Dixie Ordnance Works); Mathieson Chemical Corp., Lake Charles, La.; and Cactus Ordnance Works, Dumas, Texas. These plants have been able to produce synthetic ammonia at very reasonable cost and their operation has been highly successful. Sulfur compounds, which are troublesome impurities in ammonia synthesis gas made from coke, are not present in synthesis gas made by the hydrocarbon-steam process.

Several methods are in use for introducing nitrogen into the hydrogen gas to obtain the desired 3:1 hydrogen-nitrogen ratio for ammonia synthesis. Flue gas from the cracking furnace may be cooled, compressed and introduced with the steam and hydrocarbon in the furnace feed; hydrocarbon gas may be burned in an inert gas generator and the resulting flue gas introduced into the cracking furnace effluent; or air in the proper ratio may be introduced into the furnace effluent so that the oxygen is reacted with some of the hydrogen, leaving the proper hydrogen-nitrogen ratio.

Carbon monoxide in the ammonia synthesis gas is largely removed by converting it to carbon dioxide as has already been described for the pe-

*Presented before California Natural Gasoline Assn., Los Angeles, Aug. 5, 1948.

troleum hydrogenation plants. Carbon dioxide is removed in some cases by the Girbotol absorption process and in other cases by absorption in water after compressing the gas to 300 or 400 psi. Small concentrations of carbon dioxide remaining after the water scrubbing step are removed by further scrubbing with caustic soda solution. The small concentration of carbon monoxide remaining after the conversion step is removed by scrubbing the gas with ammoniacal copper solution or by passing it over a special catalyst or spent ammonia synthesis catalyst to react the carbon monoxide with hydrogen to form water vapor and methane.

This step is usually termed methanation and the reaction is the reverse of reaction 1 above. Thus, conventional ammonia synthesis gas made from hydrocarbons and steam consists essentially of a 3:1 mixture of hydrogen and nitrogen with a small percentage of methane as impurity. The methane is separated by purging after the ammonia has been synthesized and liquefied.

Synthesis of ammonia is carried out over a catalyst at about 800° F. and at a pressure of approximately 4500 psi. in some plants.

In other plants the pressure is held at approximately 14,000 psi. At the lower reaction pressure considerably more recycling of the synthesis gas over the ammonia catalyst is required, but in both cases utilization of the hydrogen-nitrogen mixture is virtually complete and only a small amount of gas is purged to rid the system of accumulated methane, argon, and other fixed gases.

High-Purity Hydrogen

The hydrocarbons used in the plants mentioned above have been natural gas and refinery gases, both of which are normally gaseous mixtures. Several years ago, the Girdler Corp. adapted the hydrocarbon-steam process to the production of hydrogen of high purity, utilizing propane and butane as process materials so that hydrogen plants could be built in locations in which natural gas or refinery gases are not available. In addition to their relatively greater availability, propane and butane are advantageous process materials for use in cases in which it is necessary to produce hydrogen entirely free from nitrogen since much of the natural gas in the country does contain some nitrogen which appears in the finished hydrogen. Where suitable natural gas is available, however, high-purity hydrogen can be, and is, produced by this process. Pilot plant work on the use of hydrocarbons in the gasoline range and heavier for feed material to steam-hydrocarbon furnaces is now being conducted by the Girdler Corp.

High-purity hydrogen has found its principal use in the hydrogenation of various animal and vegetable oils in the presence of nickel catalysts. In such operations, it is necessary to use hydrogen substantially free from carbon monoxide since this impurity is a catalyst poison under the conditions employed in such hydrogenations. It is also necessary for the hydrogen to be entirely free from sulfur compounds. Both of these impurities are effectively eliminated from the finished hydrogen during its production.

A typical plant for the production of high-purity hydrogen from propane or butane will consist of the following sections:

1. Hydrocarbon handling and purification
2. Hydrogen production
3. Hydrogen purification
4. Amine reactivation
5. Hydrogen compression and storage

The flow diagram from Girdler's Hygirtol hydrogen manufacturing plant is shown in Fig. 1. A plant of this type will produce hydrogen of sufficient purity to be utilized in all applications requiring pure hydrogen except for those few specialized uses such as the heat treating of vacuum tube electrodes in which traces of carbon compounds cannot be tolerated. Hygirtol plant hydrogen can, however, be further purified so as to be suitable for this use also.

The storage and handling of propane and butane is carried out in the same manner as is done in ordinary LPG installations. Storage tanks of such size are provided that tank car shipments of liquid hydrocarbons may be unloaded and stored. Conventional vaporizers are employed to vaporize the liquid hydrocarbon as needed.

Since commerical propane and butane may contain traces of sulfur

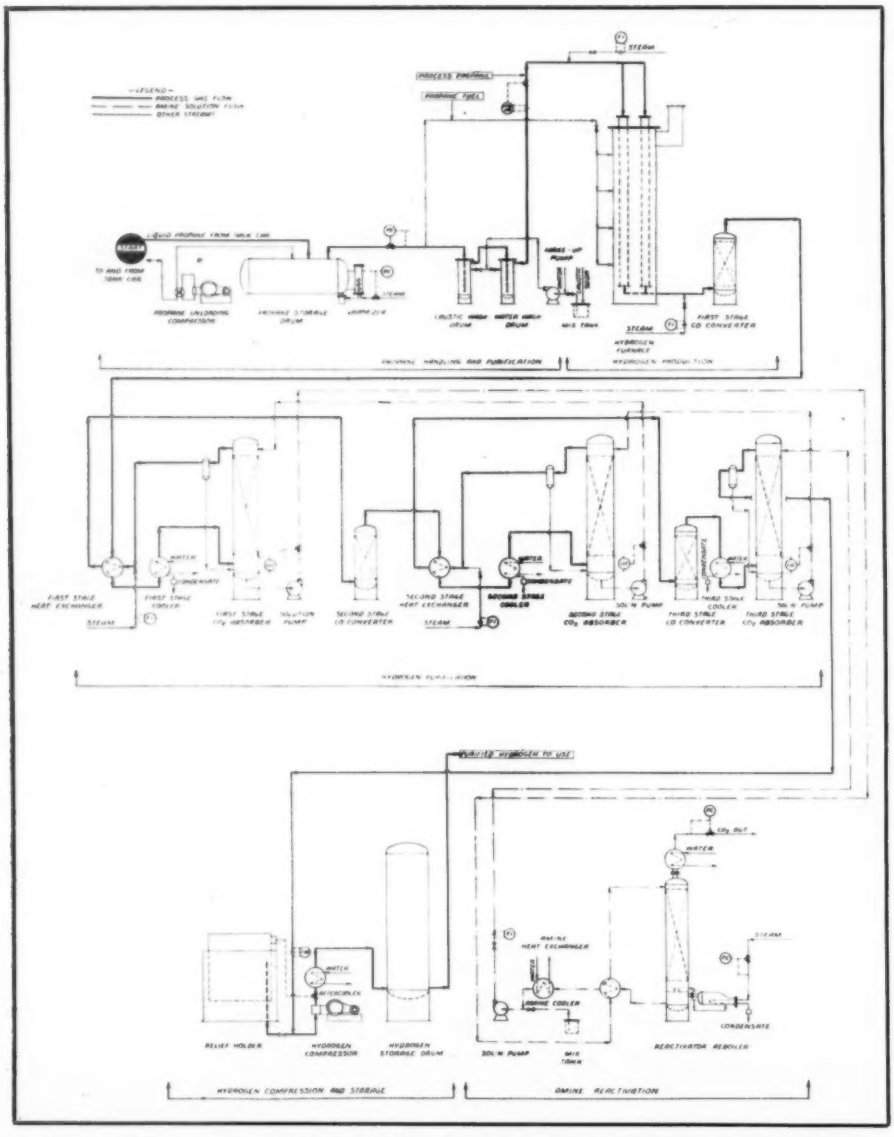
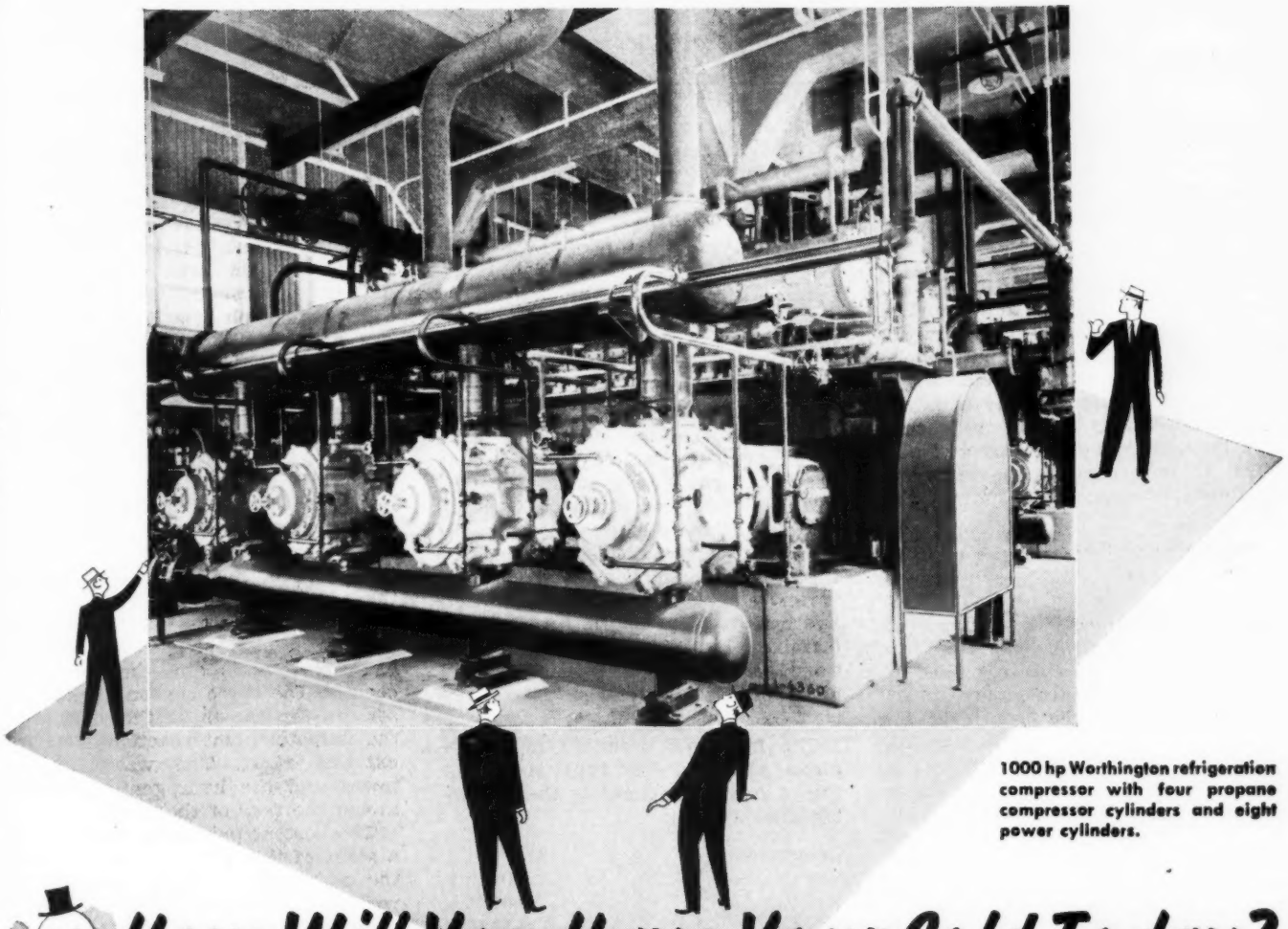


Fig. 1—Flow diagram of the Girdler Hygirtol hydrogen manufacturing plant



1000 hp Worthington refrigeration compressor with four propane compressor cylinders and eight power cylinders.

How Will You Have Your Cold Today?

Some buying notes on refrigeration compressors in the 150 to 1000 tons range

The right size. For anything between 150 to 1000 tons . . . between 400 and 1000 bhp . . . you'll find a Worthington gas engine-driven compressor that hits your requirements on- or close to-the-nose.

The right design. It will be compact and well-balanced, with compressor and power cylinders mounted on an angle-type frame, using a common large-diameter crankshaft.

The right construction. Such features as solid bore power cylinders (fully jacketed with directed water to hottest parts) and heat-treated steel forged connecting rods.

The right lubrication. Full pressure feed to bearings, cylinders and packing . . . cast-in oil manifold . . . connecting rods rifle-drilled for lubrication.

The right packing. Exceptionally deep packing boxes fitted with metallic full-floating type piston rod packing —vented and lubricated.

The right valves. Large area Worthington Feather* Valves—lightest, tightest, quietest ever made—in suction and discharge.

The right "easy-maintenance" features. Power and compressor rods identical and interchangeable . . . shim-adjustable babbit-lined steel main and crankpin bearings . . . famous Worthington easy-on, easy-off, always-tight QD sheaves.

The right safety features. Shutdown controls for overspeed, oil pressure failure, excessive water jacket temperature.

In a word—it's the *right* machine for the job, demonstrating again that *there's more worth in Worthington.* Bulletin C-1100-B21 tells more; address *Worthington Pump and Machinery Corporation, Harrison, New Jersey.*

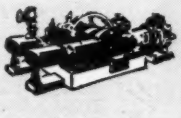
WORTHINGTON

AB-34

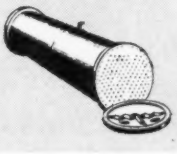
*Reg. U. S. Pat. Off.

FIVE MORE REASONS WHY WORTHINGTON LEADS IN INDUSTRIAL REFRIGERATION

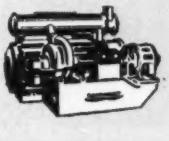
Horizontal compressors for all types of refrigerants



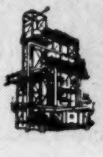
Shell and tube refrigerating equipment



Centrifugal compressors



Absorption refrigerating machines



Chilling machines and exchangers

compounds, either present as impurities or added as odorants, it is necessary to desulfurize these materials before they are utilized for hydrogen production. Several simple methods are available for effecting this desulfurization. In Fig. 1 a caustic wash and water wash are employed. This method is suitable for removing traces of mercaptans such as might be present in propane or butane obtained from natural gasoline. When handling materials obtained from refinery operations which may contain impurities such as carbonyl sulfides, it is necessary to employ a catalytic process for treating the feedstock.

The hydrogen production section of the plant consists of the hydrogen furnace itself containing vertical alloy steel tubes filled with a supported nickel catalyst through which the hydrocarbon-steam mixture is passed at a temperature of about 1400 to 1600° F. At the outlet of the furnace, steam is added to the product gas stream to cool it to about 700° F. before it enters the first-stage converter where most of the carbon monoxide is converted into carbon dioxide and hydrogen. From the outlet of the converter, the hot product gases pass through the first-stage heat exchanger, then through a cooler and into the first-stage carbon dioxide absorber. In this absorber, the carbon dioxide present in the gas mixture is removed by scrubbing with aqueous monoethanolamine solution.

The product gas leaving the absorber is mixed with steam, passed back through the first-stage heat exchanger to reheat it to 700°F., and then passed through the second-stage carbon monoxide converter in which more of the carbon monoxide present in the gas reacts to produce carbon dioxide and hydrogen. The hot gases from the converter pass through another heat exchanger and cooler and then enter the second-stage carbon dioxide absorber.

Here again carbon dioxide is removed from the gas stream by scrubbing with the monoethanolamine solution and the purified gas is again mixed with steam, passed through the heat exchanger and into the third-stage carbon monoxide converter. On the outlet of this converter the gas stream passes through a final cooler and into the third-stage carbon dioxide absorber in which the carbon dioxide produced in the third-stage carbon monoxide converter is scrubbed from the purified hydrogen stream by the monoethanolamine solution. Methanation, mentioned above, is sometimes used in place of the third stage of conversion.

The hydrogen produced in a Hygirtol plant of the type shown in Fig. 1 has approximately the following analysis:

Component	Mol %
CO_2	0.01
CO	0.01
CH_4	0.10
N_2	0.01
O_2	0.00
H_2	99.87
	100.00

Hydrogen of this purity has been found suitable for use in the hydrogenation of edible oils and in other operations where high-purity hydrogen is required.

The carbon dioxide removal in this hydrogen plant is effected in a typical Girbotol unit in which the monoethanolamine solution is reactivated by steam stripping in a packed or plate reactivator tower and in which the absorption is carried out in three stages with the same solution being used in series in the three absorbers.

A photograph of a Hygirtol hydrogen plant of the type just described is shown in Fig. 2. At the left may be seen two caustic scrubbers and a water scrubber for removing sulfur compounds from the process propane. The top flanges of the two underground propane storage tanks may be seen in the left foreground with the propane vaporizer appearing just behind them. The hydrogen furnace is shown in the left rear portion of the picture while the three carbon monoxide converters may be seen in the center just behind the two gas heat exchangers and the three gas coolers. The three carbon dioxide absorbers are shown at the right with the Girbotol plant reactivator at the extreme right. The water cooling tower and the hydrogen gas holder are in the rear of the picture.

The cost of producing hydrogen in a plant of this type will depend upon the cost of the process materials as well as utility and labor costs. The process material and utility requirements for producing pure hydrogen in a typical Hygirtol plant are given in Table 1. The operation of the plant is continuous and requires only part-time supervision by one attendant. In most locations, the major equipment can be placed outdoors as shown in the plant in Fig. 2.

Pure carbon dioxide is obtained as a byproduct in Hygirtol plant operation. This amounts to approximately 35 lbs. of carbon dioxide per 1000 cu. ft. of hydrogen produced. By the addition of scrubbing and compression equipment, liquid carbon dioxide may be recovered for sale or use. The carbon dioxide gas produced by the plant is also suitable for firefighting, purging and blanketing operations.

Another important use for high-purity hydrogen is in the preparation of anhydrous hydrogen chloride for plastics manufacture and other purposes. Although hydrogen and chlorine as made in the conventional electrolytic process can and are being used directly for this purpose, it has

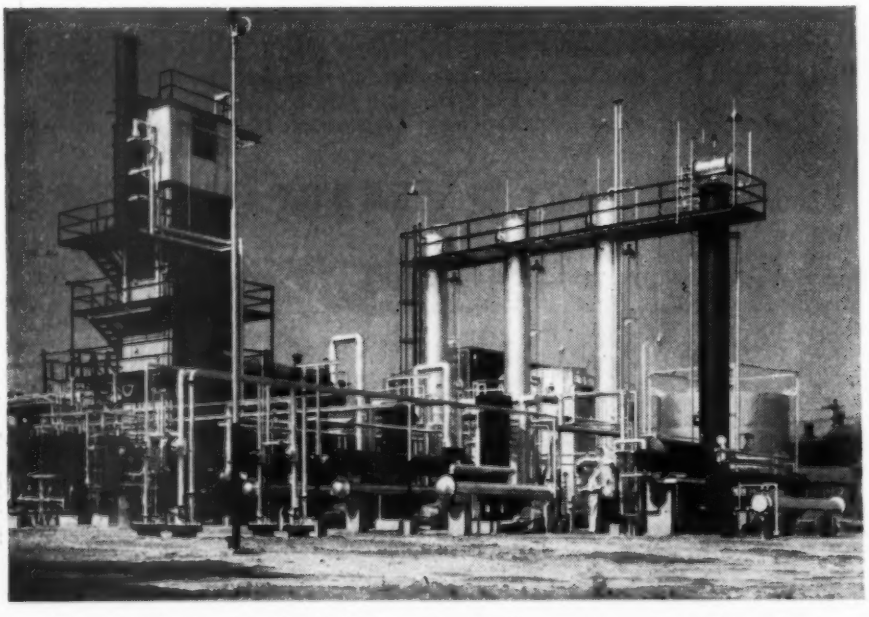


Fig. 2—Girdler Hygirtol high purity hydrogen manufacturing plant

TABLE 1—Process Material and Utility Requirements in a Typical Hygirtol Plant

(Per 1000 cu. ft. of pure hydrogen)

Material	Quantity per MCF of H_2
Process Material	
Propane, gals.	2.75
Natural gas, cu. ft.	250
Fuel (gas or oil), Btu	250,000
Steam, lbs.	380
Cooling Water (30 F. rise) gals.	1600
Power, KWH	2
Chemicals, ¢	2

turned out to be more economical for some plant locations to have chlorine shipped in by tank car and to prepare hydrogen gas separately from propane which is also shipped in by tank car.

A third use for high-purity hydrogen is in the synthesis of organic chemicals derived from light petroleum hydrocarbons. A large chemical plant near Bishop, Texas, is now using substantial quantities of high-purity hydrogen in the synthesis of a number of organic chemicals.

At the present time, there are some 10 Hygirtol high-purity hydrogen plants in operation with an equal number in various stages of construction. In size, some of these plants are smaller than the petroleum hydrogenation or the ammonia synthesis gas plants, having daily hydrogen production rates ranging from about 100,000 to 1,000,000 standard cu. ft./day. The rapidly increasing number of these plants attests to their economy and efficiency. Designs have been developed for much larger plants of this type and designs are being completed for smaller plants to satisfy the needs of some small users of hydrogen, particularly in the edible fats and chemical fields.

Hydrogen-Carbon Monoxide Mixtures

Since the gas mixture resulting from the steam-hydrocarbon reaction consists of carbon monoxide, carbon dioxide and hydrogen, it is possible to produce mixtures of carbon monoxide and hydrogen which are suitable for use in various synthesis operations such as the methanol and Fischer-Tropsch syntheses. In order to obtain the high $CO:H_2$ ratios required in many of these synthesis gas mixtures, it is necessary to introduce carbon dioxide into the reformer furnace to replace part or all of the steam used to react with the hydrocarbon. The following reaction is involved:

$$C_nH_{(2n+2)} + nCO_2 = 2nCO + (n + 1)H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Under many conditions the reactions can be carried out so there will be only a small amount of carbon dioxide in the product gas, but if complete carbon dioxide removal is required, this component can be removed by Girbotol scrubbing.

A synthesis gas production plant has recently been built for the Bureau of Mines at Bruceton, Pa., by the Girdler Corp. which has two furnaces. One is used in the production of pure hydrogen and the other for producing $CO:H_2$ mixtures. In order to produce the carbon dioxide necessary for use in the second furnace, natural gas is burned in an inert gas generator and the carbon dioxide is recovered from the resulting flue gases by scrubbing with amine solu-

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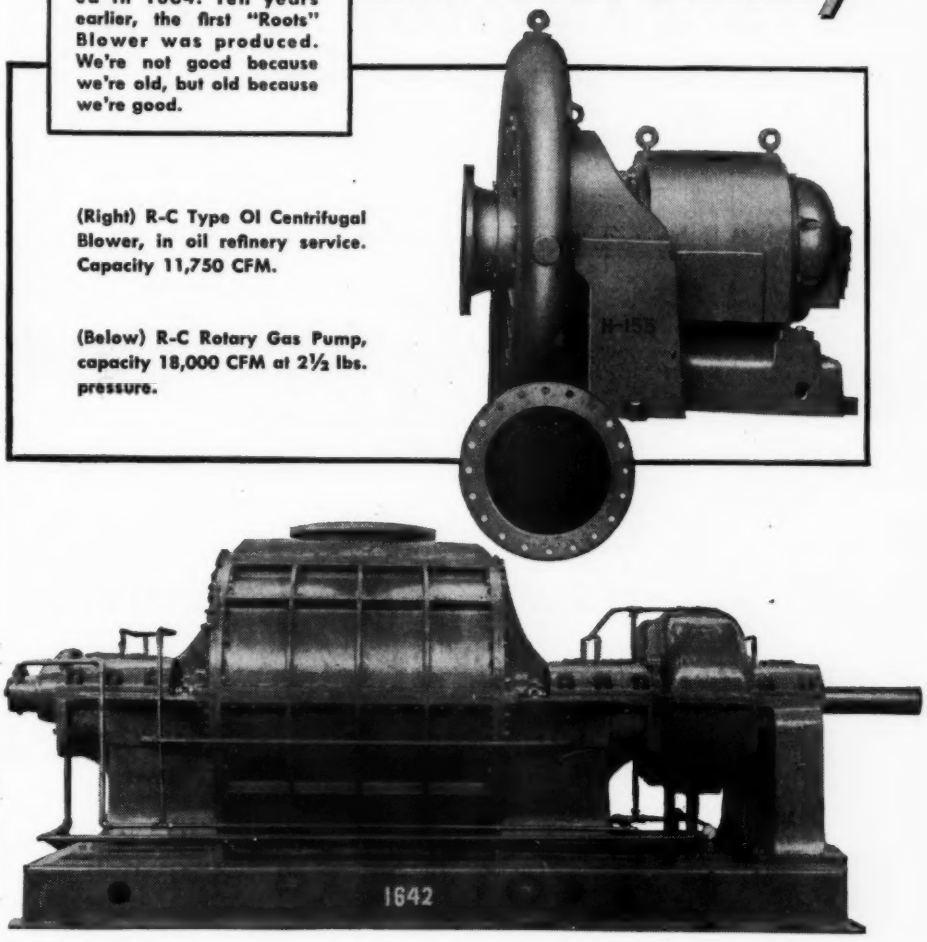
(Right) R-C Type OI Centrifugal Blower, in oil refinery service. Capacity 11,750 CFM.

(Below) R-C Rotary Gas Pump, capacity 18,000 CFM at 2½ lbs. pressure.



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tion, although the carbon dioxide could be recovered from the flue gas from the furnace itself.

In this plant $CO:H_2$ ratios as high as 10 to 1 have been produced, so that it is capable of making any desired mixture of hydrogen and carbon monoxide from pure hydrogen down to a gas containing less than 10% hydrogen and the balance carbon monoxide. By proper control of the ratios of reactants and the operating conditions in the furnace, very accurate control of the $CO:H_2$ ratio is easily attainable.

While the principal object of the Fischer-Tropsch type of plant is to produce liquid fuels, principally gasoline, from $CO:H_2$ mixtures, a considerable quantity of co-products, mainly ethanol, propanol, butanol, acetic acid, propionic acid, acetone, methyl ethyl ketone, and acetaldehyde will also be produced. These are only the more important organic chemicals that will be available from this source and it is expected that a number of more complex organic acids, alcohols and ketones will also be available, but in smaller quantities.

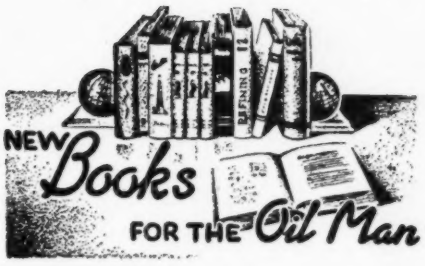
An entirely different use for $CO:H_2$ mixtures is in the reduction of various metal oxides and ores. At the present time applications of this nature are being actively explored in a number of locations.

Utility Sendout Gas

Another field in which a great deal of interest is being manifested at the present time is in the production of gas mixtures suitable for use in supplementing manufactured gas such as coke oven gas or carbureted water-gas for distribution through utility company mains.

The hydrocarbon-steam reaction has been found quite adaptable for the production of gas mixtures used for making blends equivalent to usual types of manufactured gas. The reformer furnace gas will have a very low specific gravity and a heating value of approximately 300 BTU per cu. ft. This can then be blended with propane or butane or other hydrocarbons to raise the heating value to the desired level. In some instances, a suitable blending gas can be obtained by replacing part or all of the steam in the reformer furnace with air which will produce a product gas of somewhat lower BTU content and higher specific gravity than is obtained with steam.

By various adjustments of the hydrocarbon-steam-air feed to the cracking furnace and by blending in various quantities of propane or butane, a fuel gas of almost any desired combination of gross heating value and specific gravity may be produced. Several installations of this type are already in use or under construction on the Eastern Seaboard.



Copies of all books reviewed here may be ordered from the Reader's Service Department, Petroleum Processing, 1213 West Third St., Cleveland 13, for the price listed, postpaid, unless indicated otherwise. Ohio purchasers please add 3% tax

Project 44 Data Is Included In Revised Thermodynamics Text

Introduction to Chemical Thermodynamics, 2nd Edition, by Luke E. Steiner; 6 x 9 in., 524 pages, stiff cloth binding, indexed, illustrated, $6.00. McGraw-Hill Book Co.

The first edition of Steiner's *Introduction to Chemical Thermodynamics* was published in 1941. The purposes of that volume have been retained in this new revision—to acquaint the senior student in chemistry or chemical engineering with the fundamentals of the subject, to prepare him to use current tables of data, and to give him a sound background for future work and study.

Among features of the new edition is an expansion of the chapter on gases because of the growing importance of equilibrium in the gaseous phases. The newer data on hydrocarbons published under Research Project 44 of The American Petroleum Institute and the National Bureau of Standards have been included where required in a number of chapters.

Author Steiner is professor of chemistry at Oberlin College.

Surface Reactions Conference Papers Available in Book Form

Pittsburgh International Conference on Surface Reactions, 244 pages, 8½ x 11 in., soft paper binding, illustrated, $10.00.

This book is a collection of the 28 technical papers dealing with corrosion and surface reaction phenomena that were presented at the *Pittsburgh International Conference on Surface Reactions*, June 7-11, 1948.

The material on the Conference program was organized around the following general subjects: theory of liquid phase reactions, theory of oxidation and surface reactions, preparation of surfaces, new methods and results, methods and results, fundamental mechanisms, and corrosion and its measurement.

In general the papers treat with the more theoretical aspects of corrosion, presenting probably little of immediate practical value to a plant operator. The publishers are to be highly commended for the speed in making available to the interested public a complete set of the papers for early distribution. Ordinarily, technical men have to wait overlong to see in print papers of this type if they reach the readers through the conventional channels of publication in the society journals.

Unfortunately, the book is poor typographically. It was produced by offset printing through reproduction of the author's original manuscripts. For this reason its readability in a number of pages is low.

The book was not copyrighted. That right was retained by the authors, enabling them to release their papers for further publication in any journal they might choose. The book can be obtained from the publishers, Corrosion Publishing Co., 1131 Wolfendale St., Pittsburgh 12, Pa.

Lack of Index Decreases Value Of Alkylation Patents Reference

Alkylation of Alkanes, Vol. I, Patents on Alkylation of Alkanes, by Gustav Egloff and George Hulla; 6 x 9 in., 1152 pages, stiff cloth binding, indexed, $20.00. Reinhold Publishing Corp.

This first volume in a series of three on the *Alkylation of Alkanes* comprises a collation of abstracts or digests on all available patents on this subject, U. S. and foreign, up to about June, 1947, totalling something over 800.

The patents have been classified according to processes. Catalytic alkylation is considered first, with a sub-classification based on the types of catalyst. Thermal alkylation follows; then combination processes, covering those combining alkylation with other hydrocarbon reactions. The last two divisions are on miscellaneous processes and demethylation of alkanes. No attempt is made to stress the value of specific patents. While some digests quote at greater length from the original patent than do others, this is said to be no criterion of the patent's value.

Unfortunately the book will have relatively limited use as a reference tool, for which purpose it was primarily designed, because of the lack of a proper index. The patents are *not* listed in chronological arrangement by patent number in what is called the index; this section is at most a repetition of the contents, listing each patent as it appears in the book, chronologically by page number. As a result, the reader has no easy method for locating any specific information.

MEETINGS . . . for the Oil Man

OCTOBER

4-9, American Gas Assn., annual convention, technical section, Ambassador Hotel, Los Angeles.

8, California Natural Gas Assn., 23rd annual fall meeting, Ambassador Hotel, Los Angeles.

11-13, National Lubricating Grease Institute, 16th annual convention, Edgewater Beach Hotel, Chicago.

12-16, National Chemical Exposition, Coliseum, Chicago.

14, Western Petroleum Refiners Assn., corrosion forum, Stevens Hotel, Chicago.

16, American Institute of Chemical Engineers, Oklahoma annual state meeting, Tulsa.

22-23, Measurement and Control Instrument Exposition, Municipal Auditorium, Long Beach, California.

23-29, American Society for Metals, annual convention, Benjamin Franklin Hotel, Philadelphia.

25-29, National Metal Congress and Exposition, Philadelphia.

25-29, American Welding Society, annual convention, Bellevue-Stratford Hotel, Philadelphia.

26, Independent Natural Gas Assn. of America, annual meeting, Mayo Hotel, Tulsa.

NOVEMBER

4-5, Society of Automotive Engineers, Fuels and Lubricants Division, Mayo Hotel, Tulsa.

7-10, American Institute of Chemical Engineers, Pennsylvania Hotel, New York.

8-11, American Petroleum Institute, annual meeting, Stevens Hotel, Chicago.

13-16, American Society for Testing Materials, Committee D-2 on Petroleum Products and Lubricants, Drake Hotel, Chicago.

15-18, American Oil Chemists Society, fall meeting and technical sessions, Pennsylvania Hotel, New York.

28-Dec. 3, American Society of Mechanical Engineers, annual meeting, New York.

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First stop on tour of Indiana Standard's Whiting refinery was briefing session for visitors

EQUIPMENT PERSONALS

Equipment Men Get First-Hand Picture Of How Modern Refineries Operate

TO see firsthand how their equipment and materials are used in modern refinery operations, 114 representatives of manufacturers, suppliers, and their advertising agencies toured Indiana Standard's 145,800 b/d refinery and new research laboratory at Whiting, Ind., Sept. 9.

The tour was sponsored jointly by Indiana Standard and PETROLEUM PROCESSING. It was the second such trip co-sponsored by PETROLEUM PROCESSING; on May 25 the magazine and Esso Standard Oil Co. were host to 72 eastern equipment men at Esso's Bayway, N. J., refinery.

Primary object of the tours is to afford equipment men an opportunity to observe how the equipment they advertise and sell is used, and to hear directly from refinery management how that equipment is selected and applied.

The tour started from Chicago's Loop, with the visitors being driven to the refinery grounds in chartered buses. First stop at Whiting was Indiana's recently-completed research laboratory, where a briefing session was held to inform the visitors what they would see.

They were welcomed to the plant by Conger Reynolds, public relations director for Indiana Standard, and J. C. Ducommun, refinery manager. Mr. Ducommun explained that the refinery was presently in the throes of an expansion program which would increase its capacity to 177,000 b/d. Two Fluid catalytic cracking units were recently installed, he pointed out, each with a capacity of 25,000 b/d—a far cry from the pioneer Burton stills, first built at Whiting in 1912, which processed about 100 b/d.

During the briefing session the visitors were shown an Indiana Standard movie, "Gasoline's Amazing

Guides conducted the equipment through Indiana's new research laboratory, pointing out unusual equipment and various projects that were under study

In the refinery itself the visitors were shown the control room and other accessories for the new 25,000 b/d Fluid catalytic cracking units

Molecules," which explains in live shots and animated cartoons the molecular structure of the petroleum hydrocarbons before and after cracking.

From the conference rooms the visitors were conducted in groups through the new research laboratory, and then around the refinery itself.

After lunch in the laboratory's cafeteria, the men returned to the conference room for a discussion of how Indiana Standard selects equipment for the various refineries. Speaker was Donald A. Monro, chief designing engineer of the manufacturing department.

He explained that virtually every item of equipment that is purchased must conform to specifications furnished to the supplier along with the order. For items commonly used on all the company's installations, such as piping materials, insulation, masonry materials, structural steel, paints, etc., the company generally uses its standard specifications which are given to the manufacturers, he said. Where the purchases are made by contractors, they furnish their own specifications which have been written to cover the jobs and have been approved by the company.

Buying Procedure Discussed

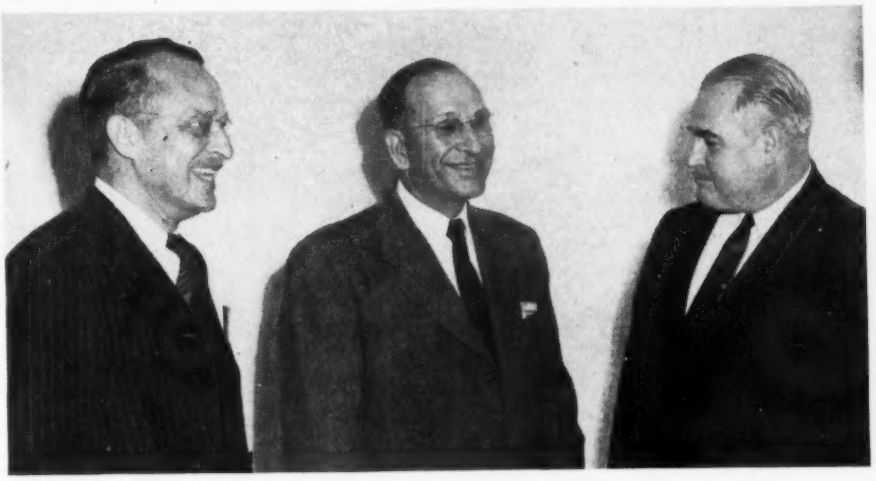
"In purchasing equipment, our regular procedure is to send the specifications out for bids to the leading manufacturers of the item, as known to our purchasers and engineers, and to obtain bids from those who are interested in quoting. The bids are then carefully analyzed and tabulated and finally the selection is made on the basis of the co-operative recommendations of the purchasing, engineering and operating departments, and in some cases the mechanical department," he said.

"In a similar manner, when equipment is purchased by one of our contractors on a cost-plus-fee basis, the contractor obtains competitive bids based on specifications that we have approved or on our own standard specifications that have been transmitted to him.

"The contractor determines the bid which in his opinion is the most preferable, and submits his recommendation to us for approval along with a tabulation of the bids and other pertinent information. Where large quantities or important materials are involved our approval of the contractor's selection is usually based on the opinions of the several departments, in a manner similar to that when we make the purchases ourselves."

Basic Rules in Purchasing

The final selection, Mr. Monro stated, is nearly always determined by five basic considerations: conformity to specifications, price, delivery, quality of the design, and reliability of the manufacturer. A half-hour question and answer period followed Mr. Monro's discussion.



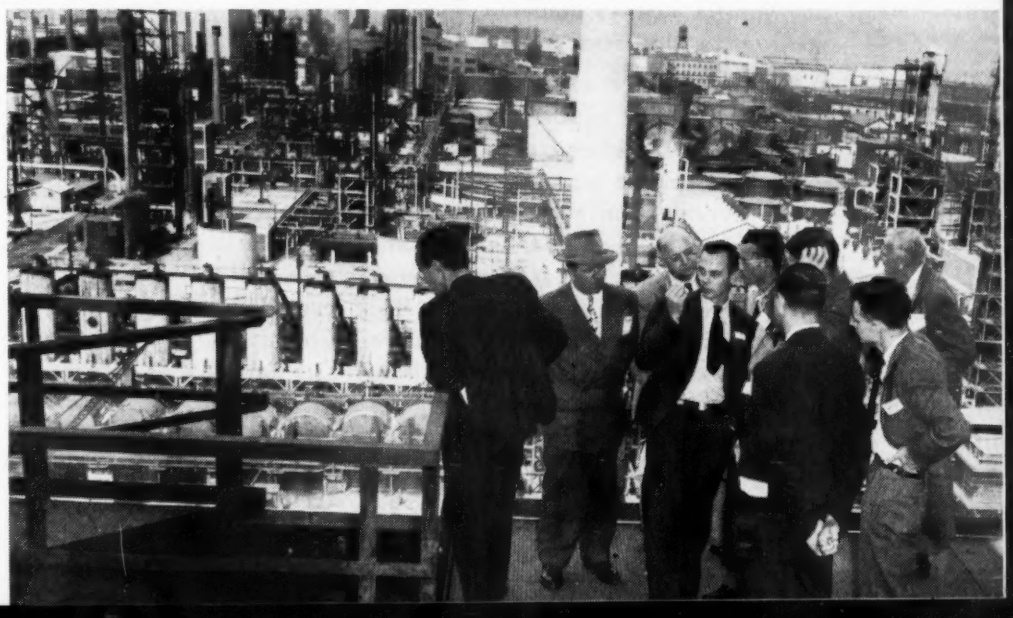
Al Wilder of Almon Brooks Wilder, Inc., and Roy Roth and E. L. Abramson of the Roy E. Roth Co. talk over what they've seen on the tour

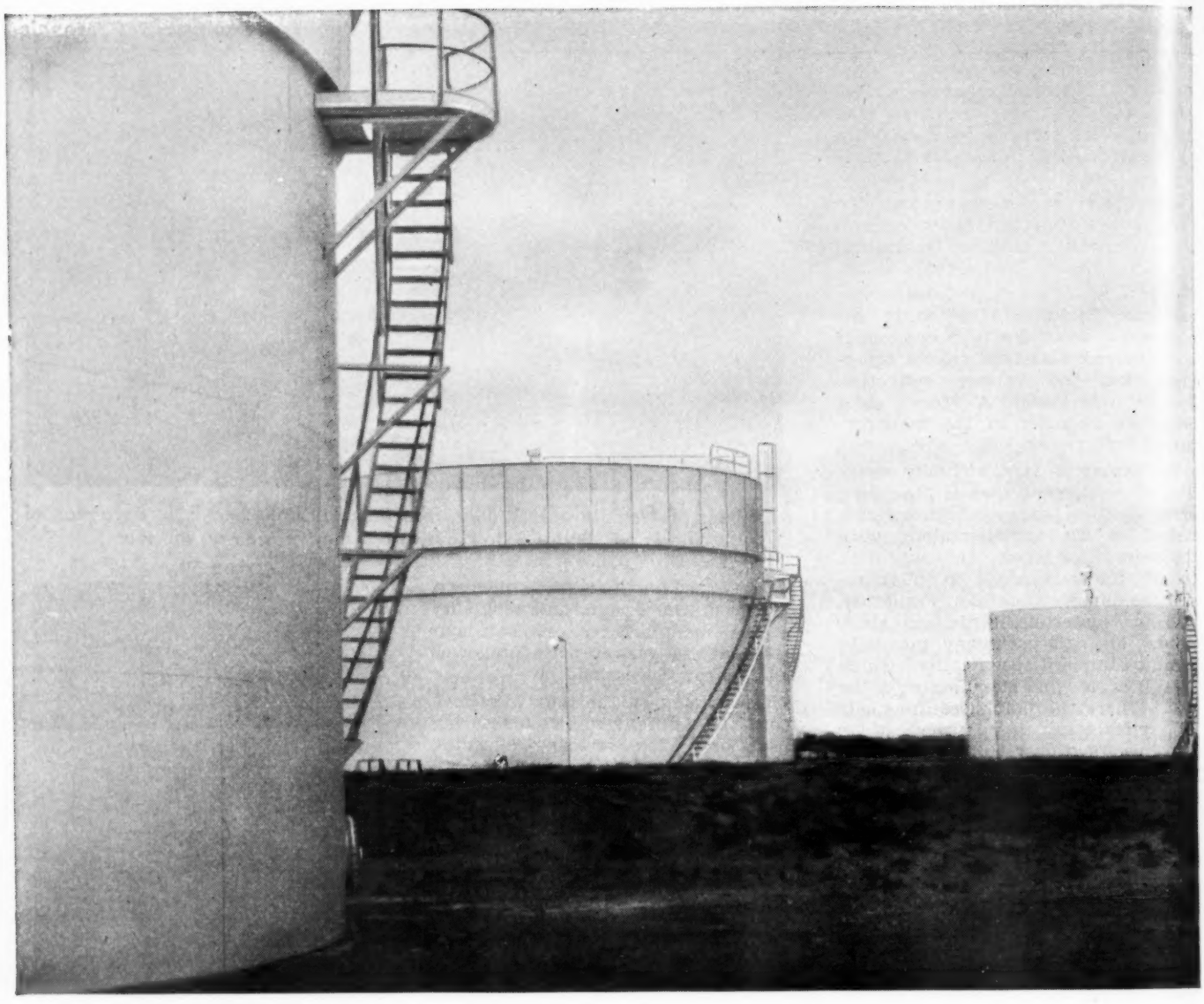
Represented on the tour were men from 24 different manufacturing firms and 12 advertising agencies, including firms as far away as Milwaukee, Cudahy, Kenosha and Racine, Wisc., and Rockford, Ill.

Manufacturers represented were Allis-Chalmers Co.; Louis Allis Co.; Ampco Metal, Inc.; Apex All-Weather Products Co.; Armour & Co.; Central Scientific Co.; Chicago Bridge & Iron Co.; Crane Co.; Crane Packing Co.; Fairbanks, Morse & Co.; Franklin Supply Co.; General American Transportation Co.; Globe Steel Tubes Co.; Ladish Co.; Magnaflux Corp.; Plibrico Jointless Firebrick Co.; Roy E. Roth Co.; Sivyer Steel Casting Co.; A. O. Smith, Corp.; Swift & Co.; Taylor Forge; Tri-Clover Machine Co.; Wheelco Instruments Co.; and Young Radiator Co.

Donald A. Monro, Indiana's chief designing engineer, who discussed equipment selection

High spot of tour was trip to top of new catalytic cracking unit, which afforded birdseye view of refinery





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PERSONALS

Petroleum Technologists in the Headlines

E. R. Baker, formerly director of development for Emery Industries, Inc., has been appointed manager of Continental Oil Co.'s newly-created Central Research Laboratories.

Mr. Baker

A graduate of Yale where he received his B.S. degree in chemistry and later did graduate work, Mr. Baker also studied at Suffolk Law School, received an LL.D. degree and became a member of the Massachusetts bar.

Prior to his association with Emery Industries, Mr. Baker was with Plymouth Co. and Quaker Chemical Products Corp. He entered the Army in 1941, and served in the chemical warfare service as assistant chief of the technical division, receiving his discharge in 1946 as a colonel with the Legion of Merit Award.

* * *

G. E. McKenna has been promoted to the position of superintendent of the Borger Refinery of Phillips Oil Co., filling the vacancy created by the death of **R. D. Evans.** Before joining Phillips in 1936, McKenna was employed by Humble Oil Co., Penna Petroleum Co., and Great Lakes Pipe Line Co. as a chemist and engineer. He graduated from Kansas University in 1930 with a B. S. degree in chemical engineering and later took post graduate work at Kansas.

* * *

T. L. Tiernan has been named manager of Sunray Oil Corp.'s refinery at Allen, Okla., succeeding **Dewey Vinson,** who has been transferred to the company's Duncan plant. Mr. Tiernan formerly was assistant superintendent, and started with Sunray in 1933 as an electrician.

Other promotions at the Allen refinery include the following: **Ault Milne,** from stillman to plant superintendent; **Luther Jones** and **Edgar Dean,** from stillmen to assistant superintendents; **Carl F. Kile** from treater to foreman of treating, blending, and loading racks; and **Herman C. Kraettli,** from engine mechanic to mechanical foreman.

* * *

Dr. Michael J. Rzasa, who received his Ph.D. in chemical engineering from the Univ. of Michigan in October, 1947, has been elevated to Research Group Supervisor in the Research Department of Stanolind Oil and Gas Company in Tulsa. Dr. Rzasa will head a new group called the Hydrocarbon Phase Equilibria Group which will handle all research pertaining to PVT and phase equilibria problems.

* * *

R. L. (Dick) Johnson has been promoted to manager of Sunray Oil Corp.'s refinery at Duncan, Okla., according to **F. L. Martin,** executive vice president in charge of refining. Mr. Johnson had been superintendent of the Duncan plant since August, 1947, and he succeeds **W. D. Manz,** resigned.

With Sunray since 1929 when the company bought the former Homaokla refinery at Allen, Okla., of which he was then superintendent, Mr. Johnson was transferred to be superintendent of Sunray's Santa Maria, Calif., refinery when it was acquired in 1946, and remained in this position until he was transferred to Duncan a year ago.

* * *

T. Ellwood Webster, president of Catalytic Construction Company, subsidiary of Houdry Process Corporation, has named **John E. Weber** as Manager of the Planning Department of Catalytic's Engineering Division.

Mr. Weber studied mechanical engineering at Pratt Institute, Brooklyn, and for nearly twenty years worked for The M. W. Kellogg Company where he rose to head of the Piping Department and Assistant to the Chief Draftsman.

Between 1943 and 1946 he served as Division Engineer with the Kellex Corporation, organizing and managing all phases of design and drafting on the Atomic Energy Diffusion Project at Oak Ridge, Tennessee. At the peak of this effort, there were 480 men on his staff.

In the following year, Mr. Weber was Oil Refinery Engineer for Arthur G. McKee Company and in the year prior to joining Catalytic Construction Company, he was Project Engineer for Project Engineering Company of New York, New York.

* * *

M. P. L. Love, director of research at Shell Oil's Wood River, Ill., refinery, has been named research department manager in the company's New York head office. In his new capacity, Mr. Love will coordinate and direct all manufacturing-research programs in the company's East-of-Rockies territory.

Mr. Love graduated from Mississippi College in 1928 and did graduate work in organic chemistry for 3½ years at the University of Virginia, completing this work in 1931. He joined Shell in 1935 as junior chemist at the Wood River refinery. After filling various research positions there and in the company's head office, he became chief research chemist at Shell's Houston laboratories in 1942, and research director in 1943. Later in 1943 he was appointed director of the Wood River research laboratories, a position he has held ever since.

R. J. Greenshields, chief engineer at the Wood River laboratories, succeeds Mr. Love as research director there.

* * *

Warren A. Beman, process products engineer in the industrial district of the Socony-Vacuum Oil Co., Inc., at Albany, N. Y., has been transferred to Socony-Vacuum's Chemical Products Division of the headquarters Lubricating Department in New York, as a staff engineer.

G. H. Hocking, formerly a process products engineer in the Philadelphia Division, will replace Mr. Beman at Albany. Mr. Beman joined the company in 1942 in the Technical Service Department, Socony-Vacuum Laboratories, Brooklyn. Prior to being assigned to the Philadelphia Division, Mr. Hocking was a member of the company's Research and Development Department at Paulsboro, N. J.

* * *

Robert B. Cragin, a vice-president of Houdry Process Corp. from 1944 until his resignation this year, has been named a vice-president of Refinery Maintenance Co., Inc., designers, engineers, and constructors for petroleum refining, natural gasoline and petro-chemical industries, with offices in Compton, Calif., and Houston, Texas.

Mr. Cragin

Prior to his service with Houdry, Mr. Cragin was assistant director of the Refining Division, Petroleum Administration for War. A graduate of Princeton University, he was process and sales engineer with M. W. Kellogg Co. before joining the government.

* * *

J. W. Loy has been appointed general superintendent of the Northwest Division of the Refining Department of Phillips Petroleum Co. Manager of the Refining Department of Wa-

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satch Oil Co. for the past year, he will be in charge of refineries at Woods Cross, Utah; Pocatello, Idaho; Spokane, Washington; and Great Falls, Montana, owned by Wasatch Oil Company and its subsidiaries. Loy joined Phillips immediately after graduation from Kansas State, where he earned a B. S. degree in chemical engineering in 1939.

* * *

C. C. Tate has been named Assistant Manager of the Refining Department of Phillips Petroleum Co. His new position includes supervision of the Phillips Oil Co. refineries, the Alamo Refining Co. (a Phillips subsidiary), the Wasatch Oil Co., Inland Empire Refineries, and Home Oil and Refining Co.

Tate also will continue in charge of Phillips activities in connection with the Petroleos Mexicanos project, a duty he has performed since February, 1945, in Mexico City. A 1927 graduate of Kansas State with a B. S. degree in electrical and mechanical engineering, Tate was with General Electric for five years and Texas Pacific Coal and Oil six months before joining Phillips in 1932.

* * *

Claude E. Swift, manager of research and patent counsel for Union Oil Co. of California, has been elected vice president of the company in charge of research and patents. Swift joined Union in 1926 as a seniora inspector in the research department of the Wilmington refinery. Later he served as junior chemist and assistant chemist, and in 1930 was appointed chemical engineer in the patent division. He became a patent engineer in 1934, assistant patent counsel in 1938, and patent counsel in 1939. He was appointed manager of research and patent counsel in July 1947.

* * *

Harold A. Beatty has been appointed to the newly created position of assistant director of research at the Ethyl Corp., research laboratories in Detroit. He was previously technical assistant to the general manager at the Ethyl Laboratories.

* * *

Dr. Carl F. Prutton, formerly head of the department of chemistry and chemical engineering at Case Institute of Technology, has joined Mathieson Chemical Corp. as Director of Research. He will have headquarters in Mathieson's executive offices in New York and at the research laboratories in Niagara Falls.

Dr. Prutton is widely known in the petroleum and chemical industries, having served as a consultant to the Lubrizol Corp. from 1928 until he joined Mathieson and a consultant to Dow Chemical Company from 1928 until 1941. He holds over a hundred patents on petroleum products, chemical processes and plastics.

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Position Wanted

CHEMICAL ENGINEER, Masters Degree MIT, 20 years experience oil refinery design, operation, maintenance, construction and management. Age 41. Will go anywhere but prefer warm climate. Available January first. BOX 27.

Positions Open

CHEMIST or CHEMICAL ENGINEER

Unusual opportunity with large chemical manufacturing company for experienced engineer having sound knowledge of petroleum catalyst and catalyst testing. Experience in process design and plant operation desirable. Will act as liason between production and marketing group. Prefer man with good contacts in petroleum industry where technical experience and knowledge are recognized. State present occupation and salary requirements.

Desired applicant undoubtedly is employed so that all communications will be strictly confidential.

BOX 26

POSITIONS OPEN

Large independent oil company has a number of desirable openings in its Refining Division for qualified individuals of five to fifteen years experience in refining field as follows:

1. Supervision—thermal and catalytic cracking
2. Supervision—modern lube oil refinery, propane, M.E.K., phenol
3. Supervision — general refinery maintenance
4. Equipment Inspectors

Applicant please supply resume of experience, photo and expected salary in initial reply.

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EDITORIAL VIEWPOINTS...

Opinions and Comments on Current Topics

Petroleum Research Frees Housewives From Saving Waste Cooking Fats

SHELL Chemical Corp.'s new synthetic glycerine plant at Houston, formally opened Sept.. 16, is a remarkable tribute to oil company research.

The project was started 20 years ago because someone refused to believe what was published in the chemical textbooks of that time. Its first step had to establish that a chlorine atom could be substituted, rather than added, to an olefinic petroleum hydrocarbon without destroying its characteristic double bond. This was accomplished by finding, through the work of many years, the right combination of concentration of propylene and chlorine, temperature, pressure, purity of ingredients and other factors.

The research director who started the project left the Shell company, but the work went on in the hands of other young men, who also refused to accept what at the time was considered an established principle of organic chemistry.

When the research was successfully completed, it was necessary to wait eight years more until economic conditions permitted construction of the present commercial unit. The fact that the manufacture of synthetic detergents today is cutting into production of soaps and fatty acids adds to the significance of the development, for glycerine up to the present has been a by-product of soap and fatty acid manufacture.

But probably the greatest significance of Shell's new glycerine plant to the greatest number of people is that it heralds the emancipation of American housewives from the odious chore of saving their cooking fats and greases when an emergency demand for glycerine arises. As fast as plants can be built, glycerine can be synthesized from propylene to meet any emergency or peacetime requirement that might arise.

Safety Record Improves Despite Complex Nature of Refining Today

THE DEPARTMENT OF SAFETY of the American Petroleum Institute has performed another valuable service for the refining industry. Through the work of its Medical Advisory Committee, it has prepared and made generally available in bulletin form accurate and concise data on the toxic properties of the chemical substances handled and used in volume in the modern refinery.

The evolution of petroleum refining from a relatively simple process of thermal distillation and acid treatment of products to a variety of complex catalytic cracking and numerous other involved processes now calls for the use of a large number of chemicals as catalysts and in product treating. The bulletins provide valuable data on toxic properties, treatments following exposure, and precautionary measures in handling the substances.

Since attention is thus called to the complex nature of present-day refining, it is not amiss to point also to the steadily improving safety record of the refining industry. While more of the toxic substances are being used in processing, the precautions taken in the plants for handling them, such as special containing vessels and closed processing systems, have made it possible for the companies more adequately to safeguard the safety and health of their workers than even a decade ago. The accident frequency rate from all causes for 1947 in refineries of 9.16 disabling injuries per 1,000,000 hours worked is the lowest in five years. It is the lowest in any branch of the petroleum industry and is well under the average for all industry.

High-class engineering in the design and construction of modern processing units has contributed to this excellent injury record, which the accident prevention programs in refineries so faithfully maintain and improve.

What Do You Know About D-2, CRC And Our Other Technical Groups?

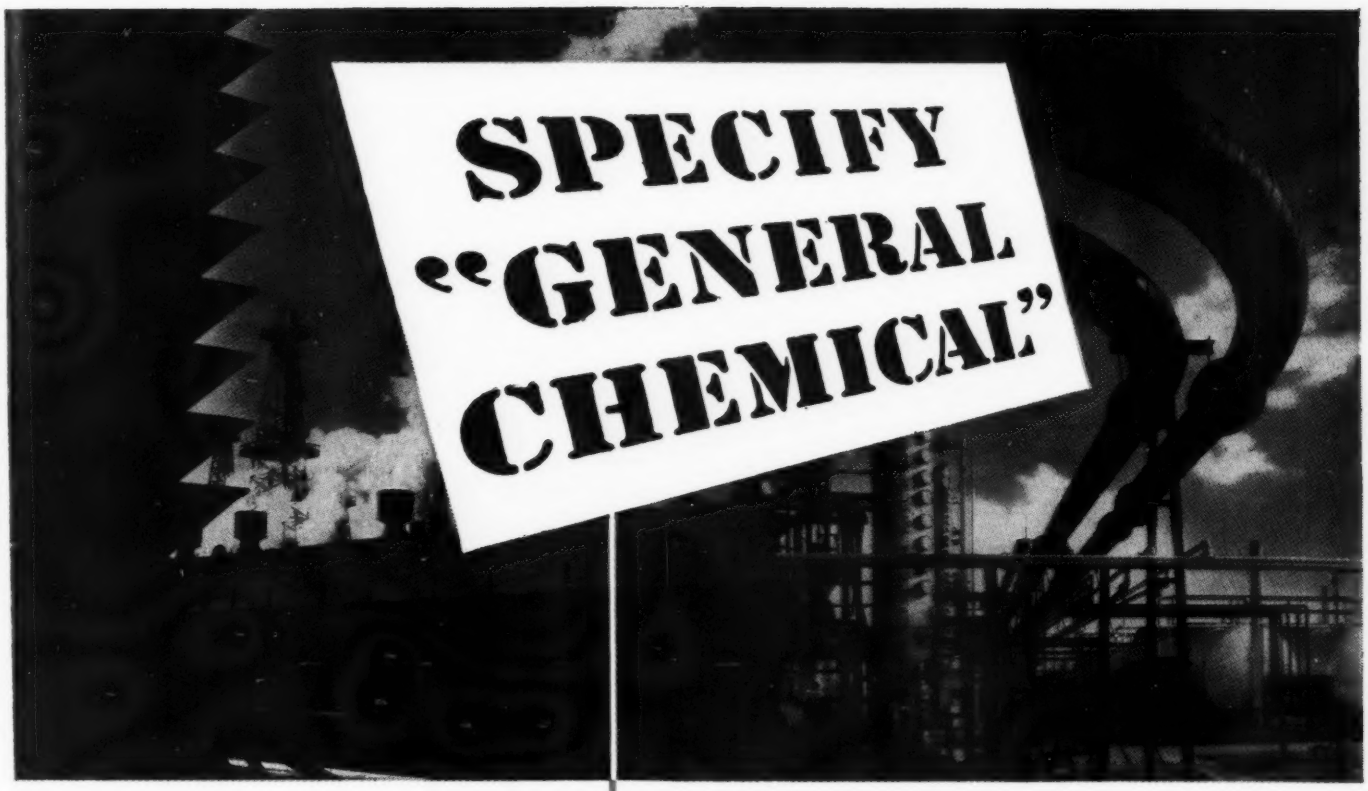
IT is a safe bet that one could go through the offices and plant operating forces of almost any refinery and find but a few men who know what the symbols D-2 and CRC stand for, much less appreciate how their work has contributed to the technological progress of the petroleum refining industry.

The above thoughts were called to mind when a representative of Committee D-2, on Petroleum Products and Lubricants, of the American Society for Testing Materials, appeared before a recent meeting in Cleveland of the National Petroleum Assn., to review the committee's current activities in promoting the standardization of test methods and product specifications.

Important too was the fact that the speaker, H. P. Ferguson, chief of the Refining Control Division, Standard Oil Co. (Ohio) is chairman of D-2's Public Relations Sub-committee. For this would indicate that this one technical group at least is aware of the need to get the story of what it is doing before the general refining industry. Without doubt the refinery executives, plant supervisors and others who heard Mr. Ferguson's talk carried away a better understanding of Committee D-2 and its work than they ever had before.

The Coordinating Research Council, the non-profit research organization sponsored jointly by the petroleum and automotive industries, is a technical group currently engaged in test work in the wide field involving fuels and lubricants used in automotive engines of all types. A representative of this group could well come before the general petroleum associations occasionally to tell in general terms what it is doing. From the same forums representatives of the API Committees on Refinery Waste Disposal, Corrosion Prevention and others engaged in important work on refinery technical problems could tell their stories to audiences representative of the entire industry.

This would be one way for the technical groups to cultivate the better industry relations which they recognize as needed for greater progress in their work.



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Oil Well Acidizing: Muriatic Acid, Fluoboric Acid, Hydrofluoric Acid

Detergents: Sodium Metasilicate, Disodium Phosphate, Anhydrous, Trisodium Phosphate, Tetrasodium Pyrophosphate, Anhydrous

Treating Agents: Aluminum Sulfate

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